EPA Region 5 Records Ctr
349991

MULTI-AREA QUALITY ASSURANCE PROJECT PLAN

12th Street Landfill Site (Operable Unit No 4) and Plainwell Mill Site (Operable Unit No 7)

Allied Paper, Inc /Portage Creek/
Kalamazoo River Superfund Site
Allegan County, Michigan

Revision 03, Addendum 04
September 23, 2009

Submitted in connection with Phase II Remedial Investigation Work Plan, Plainwell Mill and the Remedial Action Work Plan, 12th Street Landfill

Prepared by Conestoga-Rovers & Associates
on behalf of Weyerhaeuser Company

SEPTEMBER 2009
REF NO 56394 (3)
This report is printed on recycled paper

Prepared by
Conestoga-Rovers
& Associates

261 Martindale Rd Unit #3
St Catharines Ontario
Canada L2W 1A2

Office 905 682 0510
Fax 905 682 8818

TABLE OF CONTENTS

			Page
1 0	INTRODUCTION		1
	1 1	DEVELOPMENT OF THE MULTI-AREA QAPP	2
	1 2	PROJECT SETTING	2
	1 3	APPLICABILITY OF THE MULTI-AREA QAPP	3
2 0	SCOPE OF ACTIVITIES		5
	2 1	EMERGENCY RESPONSE ACTIVITIES AT THE 12TH STREET LANDFILL (OPERABLE UNIT NO 4)	6
	2 1 1	FORMER POWERHOUSE DISCHARGE CHANNEL	6
	2 1 2	EASTERN BANK OF THE LANDFILL	7
	2 2	EMERGENCY RESPONSE ACTIVITIES AT THE FORMER PLAINWELL MILL BANKS (OPERABLE UNIT NO 5)	8
	2 3	PREDESIGN INVESTIGATIONS FOR THE REMEDIAL DESIGN FOR THE 12TH STREET LANDFILL (OPERABLE UNIT NO 4)	9
	2 3 1	EXTENT OF PAPER RESIDUALS BEYOND LANDFILL FOOTPRINT	11
	2 3 2	GRADING DESIGN	13
	2 3 3	LANDFILL GAS MANAGEMENT	13
	2 4	RI/FS AT THE PLAINWELL MILL (OPERABLE UNIT NO 7)	14
	2 4 1	PHASE 2 OF ADDENDUM NO 1	14
	2 4 2	PLAINWELL MILL RI/FS – PHASE I INITIAL GROUNDWATER ASSESSMENT	15
	2 4 3	PLAINWELL MILL PHASE II RI WORK PLAN	16
	2 5	REMEDIAL ACTION WORK PLAN AT 12TH STREET LANDFILL (OPERABLE UNIT NO 4)	23
	2 5 1	EXCAVATION ACTIVITIES	23
3 0	DOCUMENT OVERVIEW		24
4 0	REFERENCES		25

LIST OF FIGURES
(following text)

FIGURE	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
FIGURE 1 1	November 2008	SITE LOCATION MAP	Rev 02 Add 03
FIGURE 1 2	November 2008	ALLIED PAPER INC /PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE	Rev 02 Add 03
FIGURE 2 1	November 2008	HISTORICAL SAMPLING DATA FOR THE FORMER POWERHOUSE DISCHARGE CHANNEL	Rev 02 Add 03
FIGURE 2 2	November 2008	PROPOSED WETLAND WOODLAND AND ASPHALT PLANT AREA INVESTIGATIONS	Rev 02 Add 03
FIGURE 2 3	November 2008	PROPOSED LANDFILL PREDESIGN INVESTIGATIONS	Rev 02 Add 03
FIGURE 2-4	September 2009	PLAINWELL INC MILL SITE PLAN	Rev 03 Add 04
FIGURE 2 5	September 2009	12TH STREET LANDFILL SITE PLAN	Rev 03 Add 04
FIGURE 2 6	September 2009	PLAINWELL INC MILL AREA 1 SAMPLE LOCATIONS	Rev 03 Add 04
FIGURE 2-7	September 2009	PLAINWELL INC MILL AREA 2 SAMPLE LOCATIONS	Rev 03 Add 04
FIGURE 2 8	September 2009	PLAINWELL INC MILL AREA 3 SAMPLE LOCATIONS	Rev 03 Add 04

LIST OF ATTACHMENTS
(following text)

ATTACHMENT	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
ATTACHMENT 1 1	November 2008	LABORATORY ACCURACY AND PRECISION OBJECTIVES	Rev 02 Add 03
ATTACHMENT 1 2	November 2008	SURROGATE COMPOUND RECOVERY LIMITS	Rev 02 Add 03
ATTACHMENT 1 3	November 2008	SAMPLE CHAIN-OF CUSTODY RECORD	Rev 03 Add 04
ATTACHMENT 1 4	September 2009	LABORATORY QUALITY ASSURANCE MANUAL	Rev 02 Add 03
ATTACHMENT 1 5	September 2009	LABORATORY SOPS	Rev 03 Add 04
ATTACHMENT 1 6	November 2008	LABORATORY POLICIES AND GUIDELINES	Rev 02 Add 03

LIST OF WORKSHEETS
(following text)

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #1	September 2009	Title and Approval Page	Rev 03 Add 04
Worksheet #2	September 2009	Identifying Information	Rev 03 Add 04
Worksheet #3	September 2009	Distribution List	Rev 03 Add 04
Worksheet #4 1	April 2008	Project Personnel Sign Off Sheet (RMT)	Rev 02 Add 03
Worksheet #4 2	September 2009	Project Personnel Sign Off Sheet (WATS)	Rev 03 Add 04
Worksheet #4 3	September 2009	Project Personnel Sign Off Sheet (CAS)	Rev 03 Add 04
Worksheet #4 4	September 2009	Project Personnel Sign Off Sheet (CRA)	Rev 03 Add 04
Worksheet #5 1	September 2007	Project Organizational Chart (Emergency Response Activities for the 12th Street Landfill and the Plainwell Mill Banks)	Rev 02 Add 03
Worksheet #5 2	April 2008	Project Organization Chart (Predesign Investigations for the Remedial Design for the 12th Street Landfill)	Rev 02 Add 03
Worksheet #5 3	November 2008	Project Organization Chart (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03
Worksheet #5 4	September 2009	Project Organization Chart (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #5 5	November 2008	Project Organization Chart (12th Street Landfill Remedial Action Work Plan)	Rev 03 Add 04
Worksheet #6-1	September 2007	Communication Pathways (Emergency Response Activities for the 12th Street Landfill and the Plainwell Mill Banks)	Rev 02 Add 03
Worksheet #6 2	April 2008	Communication Pathways (Predesign Investigations for the Remedial Design for the 12th Street Landfill)	Rev 02 Add 03
Worksheet #6 3	November 2008	Communication Pathways (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #6 4	September 2009	Communication Pathways (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #6 5	September 2009	Communication Pathways (12th Street Landfill Remedial Action Work Plan)	Rev 03 Add 04
Worksheet #7	September 2009	Personnel Responsibilities and Qualifications	Rev 03 Add 04
Worksheet #8	September 2009	Special Personnel Training Requirements	Rev 03 Add 04
Worksheet #9 1	June 2007	Project Scoping Session Participants Sheet (May 8 2007)	Rev 02 Add 03
Worksheet #9 2	June 2007	Project Scoping Session Participants Sheet (June 6 2007)	Rev 02 Add 03
Worksheet #9 3	April 2008	Project Scoping Session Participants Sheet (December 7 2007)	Rev 02 Add 03
Worksheet #9 4	September 2009	Project Scoping Session Participants Sheet (January 9 2008)	Rev 02 Add 03
Worksheet #9 5	September 2009	Project Scoping Session Participants Sheet (June 2008)	Rev 02 Add 03
Worksheet #9 6	September 2009	Project Scoping Session Participants Sheet (May/June 2009)	Rev 02 Add 03
Worksheet #9 7	September 2009	Project Scoping Session Participants Sheet (April June 2009)	Rev 02 Add 03
Worksheet #10 1	June 2007	Problem Definition DQOs (Emergency Response Activities in the Former Powerhouse Discharge Channel)	Rev 02 Add 03
Worksheet #10 2	September 2007	Problem Definition DQOs (Emergency Response on the Plainwell Mill Banks)	Rev 02 Add 03
Worksheet #10 3	April 2008	Problem Definition DQOs (Predesign Investigations for the Remedial Design for the 12th Street Landfill)	Rev 02 Add 03
Worksheet #10 4	November 2008	Problem Definition DQOs (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03
Worksheet #10 5	September 2009	Problem Definition DQOs (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #10 6	September 2009	Problem Definition DQOs (12th Street Landfill RA Work Plan)	Rev 03 Add 04
Worksheet #11 1	September 2007	Project Quality Objectives/Systematic Planning Process Statements (Emergency Response Activities in the Former Powerhouse Discharge Channel)	Rev 02 Add 03

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #11 2	September 2007	Project Quality Objectives/Systematic Planning Process Statements (Emergency Response on the Plainwell Mill Banks)	Rev 02 Add 03
Worksheet #11 3	April 2008	Project Quality Objectives/Systematic Planning Process Statements (Predesign Investigations for the Remedial Design for the 12th Street Landfill)	Rev 02 Add 03
Worksheet #11 4	November 2008	Project Quality Objectives/Systematic Planning Process Statements (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03
Worksheet #11 5	September 2009	Project Quality Objectives/Systematic Planning Process Statements (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #11 6	September 2009	Project Quality Objectives/Systematic Planning Process Statements (12th Street Landfill RA Work Plan)	Rev 03 Add 04
Worksheet #12 1	September 2009	Measurement Performance Criteria (PCBs Surface Water)	Rev 03 Add 04
Worksheet #12-2	September 2009	Measurement Performance Criteria (Wet Chemistry - Surface Water)	Rev 03 Add 04
Worksheet #12-3	September 2009	Measurement Performance Criteria (PCBs Soil/Sediment)	Rev 03 Add 04
Worksheet #12 4	September 2009	Measurement Performance Criteria (PCBs – Free Product)	Rev 03 Add 04
Worksheet #12 5	September 2009	Measurement Performance Criteria (TAL Metals – Groundwater / SPLP Metals Soil)	Rev 03 Add 04
Worksheet #12 6	September 2009	Measurement Performance Criteria (TAL Metals – Soil)	Rev 03 Add 04
Worksheet #12 7	September 2009	Measurement Performance Criteria (Cyanide – Groundwater)	Rev 03 Add 04
Worksheet #12 8	September 2009	Measurement Performance Criteria (Cyanide – Soil)	Rev 03 Add 04
Worksheet #12 9	September 2009	Measurement Performance Criteria (Low Level Mercury – Groundwater)	Rev 03 Add 04
Worksheet #12 10	September 2009	Measurement Performance Criteria (SVOCs – Groundwater)	Rev 03 Add 04
Worksheet #12 11	September 2009	Measurement Performance Criteria (SVOCs – Soil)	Rev 03 Add 04
Worksheet #12 12	September 2009	Measurement Performance Criteria (VOCs – Groundwater)	Rev 03 Add 04

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #12-13	September 2009	Measurement Performance Criteria (VOCs – Soil)	Rev 03 Add 04
Worksheet #12 14	September 2009	Measurement Performance Criteria (DRO & GRO – Soil)	Rev 03 Add 04
Worksheet #12 15	September 2009	Measurement Performance Criteria (Wet Chemistry Soil)	Rev 03 Add 04
Worksheet #12 16	September 2009	Measurement Performance Criteria (Low Level Mercury and Methyl Mercury – Surface Water)	Rev 03 Add 04
Worksheet #12 17	September 2009	Measurement Performance Criteria (PCBs– Surface Water)	Rev 03 Add 04
Worksheet #13 1	September 2009	Secondary Data Criteria and Limitations (12th Street Landfill)	Rev 03 Add 04
Worksheet #13 2	September 2009	Secondary Data Criteria and Limitations (Plainwell Mill)	Rev 03 Add 04
Worksheet #14	September 2009	Summary of Project Tasks	Rev 03 Add 04
Worksheet #15 1	September 2009	Reference Limits and Evaluation (Surface Water)	Rev 03 Add 04
Worksheet #15 2	September 2009	Reference Limits and Evaluation (Soil/Sediment)	Rev 03 Add 04
Worksheet #15 3	September 2009	Reference Limits and Evaluation (Groundwater)	Rev 03 Add 04
Worksheet #15 4	September 2009	Reference Limits and Evaluation (Free Product)	Rev 03 Add 04
Worksheet #16 1	June 2007	Project Schedule/Timeline (Emergency Response Activities in the Former Powerhouse Discharge Channel)	Rev 02 Add 03
Worksheet #16 2	September 2007	Project Schedule/Timeline (Emergency Response Activities on the Plainwell Mill Banks)	Rev 02 Add 03
Worksheet #16 3	April 2008	Project Schedule/Timeline (Predesign Investigations for the Remedial Design for the 12th Street Landfill)	Rev 02 Add 03
Worksheet #16 4	November 2008	Project Schedule/Timeline (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03
Worksheet #16 5	September 2009	Project Schedule/Timeline (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #16 6	September 2009	Project Schedule/Timeline (12th Street Landfill RA Work Plan)	Rev 03 Add 04

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #17 1	June 2007	Sampling Design and Rationale (Former Powerhouse Discharge Channel)	Rev 02 Add 03
Worksheet #17 2	September 2007	Sampling Design and Rationale (Emergency Response on the Plainwell Mill Banks)	Rev 02 Add 03
Worksheet #17 3	April 2008	Sampling Design and Rationale (Predesign Investigations for the Remedial Design For the 12th Street Landfill)	Rev 02 Add 03
Worksheet #17-4	September 2009	Sampling Design and Rationale (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 03 Add 04
Worksheet #17 5	September 2009	Sampling Design and Rationale (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #17 6	November 2008	Sampling Design and Rationale (12th Street Landfill)	Rev 02 Add 03
Worksheet #18 1	September 2007	Sampling Locations and Methods/SOP Requirements (Emergency Response Activities)	Rev 02 Add 03
Worksheet #18 2	April 2008	Sampling Locations and Methods/SOP Requirements (Predesign Investigations for the Remedial Design For the 12th Street Landfill)	Rev 02 Add 03
Worksheet #18 3	November 2008	Sampling Locations and Methods/SOP Requirements (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03
Worksheet #18 4	September 2009	Sampling Locations and Methods/SOP Requirements (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #18 5	September 2009	Sampling Locations and Methods/SOP Requirements (12th Street Landfill RA Work Plan)	Rev 03 Add 04
Worksheet #19	November 2008	Analytical SOP Requirements	Rev 02 Add 03
Worksheet #20	September 2009	Field Quality Control Sample Summary	Rev 03 Add 04
Worksheet #21	September 2009	Project Sampling SOP Reference	Rev 03 Add 04
Worksheet #22	September 2009	Field Equipment Calibration Maintenance Testing and Inspection	Rev 03 Add 04
Worksheet #23	September 2009	Analytical SOP References	Rev 03 Add 04
Worksheet #24	September 2009	Analytical Instrument Calibration	Rev 03 Add 04

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #25	September 2009	Analytical Instrument and Equipment Maintenance Testing and Inspection	Rev 03 Add 04
Worksheet #26	September 2009	Sample Handling System (WATS)	Rev 03 Add 04
Worksheet #27	September 2009	Sample Custody Requirements	Rev 03 Add 04
Worksheet #28 1	September 2009	QC Samples PCBs (Surface Water/ Groundwater)	Rev 03 Add 04
Worksheet #28 2	September 2009	QC Samples TSS (Surface Water)	Rev 03 Add 04
Worksheet #28 3	September 2009	QC Samples Phosphorus (Surface Water)	Rev 03 Add 04
Worksheet #28 4	September 2009	QC Samples PCBs (Soil/Sediment)	Rev 03 Add 04
Worksheet #28 5	September 2009	QC Samples PCBs (Free Product)	Rev 03 Add 04
Worksheet #28 6	September 2009	QC Samples TAL Metals (Groundwater)	Rev 03 Add 04
Worksheet #28 7	September 2009	QC Samples TAL Metals (Soil/SPLP)	Rev 03 Add 04
Worksheet #28 8	September 2009	QC Samples Cyanide (Groundwater)	Rev 03 Add 04
Worksheet #28-9	September 2009	QC Samples Cyanide (Soil)	Rev 03 Add 04
Worksheet #28-10	September 2009	QC Samples Low Level Mercury (Surface Water/ Groundwater)	Rev 03 Add 04
Worksheet #28 11	September 2009	QC Samples SVOCs (Groundwater)	Rev 03 Add 04
Worksheet #28-12	September 2009	QC Samples SVOCs (Soil)	Rev 03 Add 04
Worksheet #28 13	September 2009	QC Samples VOCs (Groundwater)	Rev 03 Add 04
Worksheet #28 14	September 2009	QC Samples VOCs (Soil)	Rev 03 Add 04
Worksheet #28-15	September 2009	QC Samples DRO and GRO (Soil)	Rev 03 Add 04
Worksheet #28 16	September 2009	QC Samples – Hardness (Surface Water)	Rev 03 Add 04

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #28 17	September 2009	QC Samples – Methyl Mercury (Surface Water/ Groundwater)	Rev 03 Add 04
Worksheet #28-18	September 2009	QC Samples – Phosphorus (Soil)	Rev 03 Add 04
Worksheet #28 19	September 2009	QC Samples – Ammonia – N (Soil)	Rev 03 Add 04
Worksheet #28 20	September 2009	QC Samples – Nitrate – N (Soil)	Rev 03 Add 04
Worksheet #28 21	September 2009	QC Samples – Nitrite – N (Soil)	Rev 03 Add 04
Worksheet #29	June 2007	Project Documents and Records	Rev 02 Add 03
Worksheet #30	September 2009	Analytical Services	Rev 03 Add 04
Worksheet #31 1	April 2008	Planned Project Assessments (Emergency Response Activities)	Rev 02 Add 03
Worksheet #31 2	April 2008	Planned Project Assessments (Predesign Investigations for the Remedial Design For the 12th Street Landfill)	Rev 02 Add 03
Worksheet #31 3	November 2008	Planned Project Assessments (Phase 2 of Addendum No 1 [Test Pits] and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment)	Rev 02 Add 03
Worksheet #31 4	September 2009	Planned Project Assessments (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #31 5	September 2009	Planned Project Assessments (12th Street Landfill RA Work Plan)	Rev 03 Add 04
Worksheet #32 1	April 2008	Assessment Findings and Corrective Action Responses (Emergency Response Activities)	Rev 02 Add 03
Worksheet #32 2	April 2008	Assessment Findings and Corrective Action Responses (Predesign Investigations for the Remedial Design For the 12th Street Landfill)	Rev 02 Add 03
Worksheet #32 3	September 2009	Assessment Findings and Corrective Action Responses (Plainwell Mill Phase II RI Work Plan)	Rev 03 Add 04
Worksheet #32 4	September 2009	Assessment Findings and Corrective Action Responses (12th Street Landfill RA Work Plan)	Rev 03 Add 04
Worksheet #33	September 2009	QA Management Reports	Rev 02 Add 03
Worksheet #34	September 2009	Verification (Step I) Process	Rev 02 Add 03

WORKSHEET	DATE OF LAST REVISION	TITLE	LOCATION OF LAST REVISION
Worksheet #35	September 2009	Validation (Step I) Process	Rev 03 Add 04
Worksheet #36	September 2009	Validation (Steps IIa and IIb) Summary	Rev 03 Add 04
Worksheet #37	September 2009	Usability Assessment	Rev 03 Add 04

LIST OF ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
µg/kg	micrograms per kilogram
AA	atomic absorption
ARAR	Applicable or Relevant and Appropriate Requirement
ASTM	American Society for Testing and Materials
BFB	p bromofluorobenzene
BNA	base-neutral-acid extractable
CAS	Columbia Analytical Services
CCB	continuing calibration blank
CCC	calibration check compound
CCV	continuing calibration verification
CD	Consent Decree
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
COC	Chain-of-Custody
COPC	constituent of potential concern
CRA	Conestoga-Rovers & Associates
CVAA	cold vapor atomic absorption
DFTPP	decafluorotriphenylphosphine
DI	deionized
DO	dissolved oxygen
DQI	data quality indicators
DQO	Data Quality Objective
ECD	electron capture detector
EDD	electronic data deliverable
Eh	redox
FB	field blank
FS	Feasibility Study
FSP	Field Sampling Plan
GC/MS	gas chromatograph/mass spectrophotometer
GRCC	Generic Residential Cleanup Criteria
HSP	Health and Safety Plan
ICB	initial calibration blank
ICP	inductively coupled plasma
ICPMS	inductively coupled plasma mass spectroscopy

LIST OF ACRONYMS AND ABBREVIATIONS
(Continued)

ICS	interface check samples
ICV	initial calibration verification
IDW	investigation derived waste
kg	kilogram
KRSG	Kalamazoo River Study Group
L	liter
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LRA	linear range analysis
MDEQ	Michigan Department of Environmental Quality
MDL	Method Detection Limit
MS	matrix spike
MS/MSD	matrix spike/matrix spike duplicate
MSD	matrix spike duplicate
NCP	National Contingency Plan
NIST	National Institute of Standards and Technology
NTU	nephelometric turbidity unit
OSC	On-Scene Coordinator
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
pH	negative logarithm (base 10) of hydrogen ion activity
PID	photoionization detector
PQO	Project Quality Objective
POTW	publicly-owned treatment works
PM	Project Manager
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Project Plan
QC	quality control
QL	Quantitation Limit
RASs	routine analytical service
RCRA	Resource Conservation and Recovery Act
RD/RA	Remedial Design/Remedial Action

LIST OF ACRONYMS AND ABBREVIATIONS
(Continued)

RF	response factor
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RPD	relative percent difference
RL	reporting limit
RPM	Remedial Project Manager
RSD	relative standard deviation
RT	retention time
SAP	Sampling and Analysis Plan
SAS	special analytical services
SOP	standard operating procedure
SOW	Statement of Work
SPCC	system performance check compound
SRI/FS	Supplemental Remedial Investigation/Feasibility Study
SRM	standard reference material
SW846	Test Methods for Evaluating Solid Waste 1996
TAL	Target Analyte List
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
TCRA	Time-Critical Removal Action
TEMP	temperature
TB	trip blank
TSS	Total suspended solids
U S EPA	United States Environmental Protection Agency
UFP	Uniform Federal Policy
VOC	volatile organic compound
WATS	Weyerhaeuser Analytical Testing Services

1 0 INTRODUCTION

On February 22 2005, Weyerhaeuser Company (Weyerhaeuser) entered into a Consent Decree (CD) with the United States Environmental Protection Agency (U S EPA) for the Design and Implementation of Certain Response Activities at the 12th Street Landfill site (Operable Unit No 4) and the Plainwell Mill site (Operable Unit No 7) Both sites are part of the Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund site (Figure 1-1), which is located in southwestern Michigan A Statement of Work (SOW) for the Remedial Design/Remedial Action (RD/RA) at the 12th Street Landfill site was attached to the CD A SOW for the Remedial Investigation/Feasibility Study (RI/FS) at the Plainwell Mill site was subsequently issued by the U S EPA with an effective date of August 17, 2006

In late February 2007, the U S EPA authorized a Time-Critical Removal Action (TCRA) to remove polychlorinated biphenyl (PCB)–contaminated sediment in the former Plainwell Impoundment (a section of Operable Unit #5 of the Allied Paper/Portage Creek/Kalamazoo River Superfund Site) This work was authorized through an administrative settlement agreement and Order on Consent for Removal Action (V-W-07-C 8-63) As part of the TCRA, the earthen section of the Plainwell Dam was removed and the Kalamazoo River was rerouted through the former powerhouse discharge channel The 12th Street Landfill abuts the river and is located directly downstream of the earthen section of the Plainwell Dam on the western side of the former powerhouse discharge channel The Plainwell Mill also abuts the Kalamazoo River and PCB-containing materials have been documented along the riverbank at the Mill The change in the Kalamazoo River channel will result in an increased river gradient and higher velocities upstream and along the rerouted channel (USGS, 2004 and USDA, 2004) and are expected to flush residuals in the former powerhouse discharge channel downstream and erode bank material in the area of the Mill Thus the scope of the TCRA activities included actions or occurrences that threatened releases of waste material (as defined in the CD) from both the 12th Street Landfill and the Plainwell Mill properties Since any such release may present an immediate threat to public health or welfare of the environment, Weyerhaeuser was authorized to conduct several emergency response actions in conjunction with completing the required work under the CD

The U S EPA requires that all environmental monitoring and measurement efforts mandated or supported by the U S EPA participate in a centrally managed quality assurance program Any party generating data under this program has the responsibility to implement minimum procedures to ensure that the precision, accuracy completeness and representativeness of the data are known and documented To ensure that this responsibility is met uniformly a written Quality Assurance Project Plan (QAPP) must be prepared for each project

This Multi-Area QAPP presents the objectives organization functional activities and specific quality assurance (QA) and quality control (QC) activities associated with implementing the projects that are described in Section 2 This QAPP also describes the specific protocols that will be followed for sampling, sample handling and storage chain of-custody and laboratory analysis This Multi-Area QAPP will be modified in the future as other sampling programs are identified or defined (*e g*, additional worksheets, such as Problem Definition-DQOs [Worksheet No 10], will be inserted to describe the project sampling objectives and sampling program)

1 1 DEVELOPMENT OF THE MULTI-AREA QAPP

This QAPP has been prepared in accordance with the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) Manual V1, March 2005 (U S EPA, 2005a) and the Uniform Federal Policy for Quality Assurance Project Plans, Part 2B Quality Assurance/Quality Control (QA/QC) Compendium Minimum QA/QC Activities V1 March 2005 (U S EPA, 2005b)

All QA/QC procedures performed under this QAPP will be in accordance with applicable professional technical standards U S EPA requirements, other pertinent government regulations and guidelines, and the specific project goals and requirements

1 2 PROJECT SETTING

The Allied Paper Inc /Portage Creek/Kalamazoo River Superfund site is located in southwestern Michigan The site includes five disposal areas, five paper mill properties, an approximately 80-mile stretch of the Kalamazoo River from Morrow Dam to Lake Michigan, and a 3 mile stretch of Portage Creek The primary site contaminant is PCBs

a hazardous substance and probable human carcinogen PCBs were introduced to Portage Creek and the Kalamazoo River through past discharges and disposal of PCB contaminated residuals

The 12th Street Landfill and Plainwell Mill sites are located in Allegan County Michigan (Figure 1-2) The 12th Street Landfill is located in Otsego Township (Section 24 Township 1N, Range 11W), and the Plainwell Mill is located in the City of Plainwell (Section 30, Township 1N Range 11W) Both sites are located adjacent to the Kalamazoo River, with the 12th Street Landfill located approximately 1½ miles northwest and downstream of the Plainwell Mill site The 12th Street Landfill site encompasses approximately 6 5 acres and is situated on roughly a 24-acre property that is bordered to the east by woodlands and a former hydroelectric powerhouse discharge channel on the Kalamazoo River, to the north and west by wetlands, to the south and southwest by a asphalt plant mining operation, and to the south and southeast by industrially developed lands and the Plainwell Dam (which is scheduled to be removed as part of the U S EPA-approved TCRA in 2007-2008) The Plainwell Mill site encompasses approximately 36 acres and is bordered by the Kalamazoo River to the north, the Plainwell central business district to the east, residential properties to the south, and commercial properties and the City of Plainwell wastewater treatment plant to the west

Plainwell Inc , is the current owner of the 12th Street Landfill property, although Plainwell, Inc , is a bankrupt entity with no ongoing business operations Weyerhaeuser is currently in negotiations with Plainwell Inc to take ownership of the 12th Street Landfill property The mill property has been vacant since the former Simpson Plainwell Paper Company filed for bankruptcy in 2000 The City of Plainwell is the current owner of the Plainwell Mill property, having purchased the property out of the Plainwell Mill bankruptcy in 2006 Weyerhaeuser owned and operated the mill and the landfill for approximately a 9-year period, between 1961 and 1970 During that time dewatered sludge from wastewater treatment operations was excavated from lagoons on the mill property and transported for disposal at the 12th Street Landfill site

1 3 APPLICABILITY OF THE MULTI-AREA QAPP

This Multi Area QAPP is applicable for work to be performed by Weyerhaeuser and its representatives within the Allied Paper Inc /Portage Creek/Kalamazoo River

Superfund site The work activities will include tasks conducted by Weyerhaeuser under its 2005 CD with the U S EPA as may be amended or modified at the following sites

1 12th Street Landfill (Operable Unit No 4)
2 Plainwell Mill (Operable Unit No 7)

Additional areas may be addressed in the future through modifications of this Multi-Area QAPP This QAPP may be updated to address additional emergency activities and/or to integrate applicable workplan activities as required under the CD

In September 2007 this QAPP was amended to include the removal of residuals and sediment along certain sections of the banks along the Plainwell Mill property As defined in the 2005 CD the limits of the Plainwell Mill Operable Unit (OU-7) extend to the top of the riverbank Consequently the banks of the mill property are part of the Kalamazoo River Operable Unit (OU-5)

In September 2009 the QAPP was amended to include the sampling and analysis activities associated with the Phase II RI Work Plan at the Plainwell Mill and the removal of paper residuals from outside of the landfill footprint as part of the Remedial Action (RA) at the 12th Street Landfill At that time modifications were made to the QAPP to reflect the change in Project Coordinator as defined in the 2005 CD from RMT to Conestoga-Rovers & Associates (CRA)

2 0 SCOPE OF ACTIVITIES

The subsections below provide a summary of the scope for each project conducted under this Multi Area QAPP to date as well as new projects being added in this version These projects include the following

1 Emergency response activities in the former powerhouse discharge channel at the 12th Street Landfill (as described in Revision 00 June 2007, and Revision 01 August 2007)

2 Emergency Response activities on portions of the riverbank along the Plainwell Mill (as described in Revision 02 Addendum 01 September 2007)

3 Predesign investigations for the remedial design for the 12th Street Landfill (as described in Revision 02, Addendum 02 February 2008])

4 RI/FS activities at the Plainwell Mill (as described in Revision 02 Addendum No 3 November 2008 and updated in Revision 03, Addendum No 4 September 2009)

5 Remedial Action Implementation activities at the 12th Street Landfill (added in this update to the Multi Area QAPP, Revision 03, Addendum No 4, September 2009)

The summaries of projects included in previous versions of this document have not been revised or deleted As new projects are initiated new information will be added to this Multi-Area QAPP to cover the new projects, and a new addendum number will be assigned to the document (*e g* Addendum 02 will be updated to Addendum 03, and so on) If information included in a previous version of this document is changed, a new revision number will be assigned (*e g* Revision 02 will be updated to Revision 03, and so on)

2 1 EMERGENCY RESPONSE ACTIVITIES AT THE 12TH STREET LANDFILL (OPERABLE UNIT NO 4)

Weyerhaeuser has not yet received a formal notification from the U S EPA to proceed with the 12th Street Landfill RD/RA work specified in the CD The full scope of the RA for the 12th Street Landfill generally includes the excavation of wastewater residuals present outside the footprint of the landfill (on adjacent properties and in the former powerhouse discharge channel), the relocation of the excavated material back into the landfill, the construction of a landfill cover and erosion protection measures and various environmental monitoring activities Among the paper residuals to be excavated are those present in the former powerhouse discharge channel (a backwater of the Kalamazoo River), to the extent that these residuals are visibly contiguous with the landfill

The TCRA in the Former Plainwell Impoundment includes the removal of the earthen section of the Plainwell Dam The TCRA was approved by the U S EPA in February 2007, and the specified work will be implemented by the Kalamazoo River Study Group (KRSG) in 2007 and 2008 (Arcadis BBL 2007a) Consequently Weyerhaeuser needs to conduct certain activities at the 12th Street Landfill site under Section XVII, paragraph 67 (Emergency Response), of Weyerhaeuser s CD with the U S EPA in order to accommodate the TCRA and to prevent erosion of the banks of the landfill These activities include removing visible residuals in the former powerhouse discharge channel cutting back the existing landfill slope along the river, and installing erosion protection on the eastern bank of the 12th Street Landfill consistent with the requirements of the Record of Decision (ROD)

2 1 1 FORMER POWERHOUSE DISCHARGE CHANNEL

The 12th Street Landfill is situated directly downstream of the Plainwell Dam on the same side of the river as the earthen section of the dam that will be removed as part of the TCRA After the earthen section of the Plainwell Dam is removed, the former powerhouse discharge channel (currently a backwater) will become the main channel of the Kalamazoo River This will create a larger gradient on the river with resultant higher flow velocities and greater shear stresses (*i e*, erosion potential) in the former powerhouse discharge channel and on various bank areas upstream of the current Plainwell Dam The change will also alter flood conditions near the landfill Without

action the channel rerouting will resuspend and redistribute paper residuals that are present in the discharge channel including residuals that may be contiguous with the 12th Street Landfill The modified flow is also modeled to increase shear stresses along the riverbank adjacent to the 12th Street Landfill, resulting in possible destabilization of the banks and increased erosion To prevent this from occurring, Weyerhaeuser plans to perform the following activities

- Conduct bathymetric and visual sediment assessments to determine the visual characteristics of the sediment and the depth of water in the former powerhouse discharge channel (RMT, 2007a) Use this information in conjunction with previously available information (G&M, 1994, U S EPA, 2004), to estimate the extent of visual wastewater residuals that are contiguous with the 12th Street Landfill present in the channel sediment, and subject to mobilization once the Kalamazoo River is rerouted
- Excavate visible wastewater residuals that are contiguous with the 12th Street Landfill and present in the channel sediment Dewater the sediment and treat and sample water from the dewatering process before discharge back to the Kalamazoo River Dispose the excavated sediment in the 12th Street Landfill
- Collect post-excavation confirmation samples in the former powerhouse discharge channel to confirm that wastewater residuals that are visibly contiguous with the landfill have been removed, and that PCB concentrations in the excavated area are below 4 mg/kg

The locations and concentration ranges of data collected previously at the site, as well as an indication of whether residuals were observed are illustrated on Figure 2-1

2 1 2 EASTERN BANK OF THE LANDFILL

As stated in Subsection 2 1 1 after the earthen section of the Plainwell Dam is removed the former powerhouse discharge channel will become the main channel of the Kalamazoo River This will create higher velocities and greater shear stresses (*i e* erosion potential) as well as altered flood conditions along the eastern bank of the 12th Street Landfill Without action the channel rerouting could erode mixed fill/paper residuals at the toe of the eastern landfill bank and may lead to instability of the bank

Moreover certain components of the ROD such as cutting back the sideslope of the landfill along the river and creating space for an access road along the river are more effectively and efficiently implemented in conjunction with the work in the former discharge channel Consequently Weyerhaeuser plans to perform the following activities that are required by the ROD for the 12th Street Landfill as part of an Emergency Response Action

- Cut back the existing slope of the 12th Street Landfill along the river to create a more stable angle and to provide a buffer zone to ensure that once the final cover system is installed, there is no direct contact between the paper residuals in the landfill and the Kalamazoo River/former powerhouse discharge channel, and to provide space for an access road along the riverfront The excavated mixed fill/paper residuals from the eastern bank will be disposed in a designated area on top of the 12th Street Landfill
- Install erosion protection on the newly graded eastern bank of the landfill to provide protection from a 500-year flood event

Geotechnical borings have been installed in preparation for this work (RMT 2007b) Consistent with the requirements of the ROD no environmental samples are planned in connection with the above work at the 12th Street Landfill

The final cover over the landfill, along with the other components of the landfill remedy will be designed and installed in a manner and time frame consistent with the CD

2 2 EMERGENCY RESPONSE ACTIVITIES AT THE FORMER PLAINWELL MILL BANKS (OPERABLE UNIT NO 5)

Weyerhaeuser has been authorized by the U S EPA to conduct Emergency Actions at two separate locations adjacent to the Kalamazoo River under Paragraph 67 of their 2005 CD As part of the Emergency Action for the former powerhouse channel at the 12th Street Landfill (Operable Unit 04), Multi-Area QAPP and Field Sampling Plan (FSP) were submitted and approved (approval letter from Michael Berkoff dated July 24 2007) On June 29 2007 the U S EPA also authorized Weyerhaeuser to take actions to prevent abate or minimize a release or potential release of hazardous substances from

the former Plainwell Mill banks The former Plainwell Mill banks are considered part of the Kalamazoo River operable unit (Operable Unit 05)

The following objectives have been developed for the Emergency Action along the former Plainwell Mill banks

- Remove or contain visible paper residuals and address previously identified areas of reported PCBs concentrations of greater than 50 mg/kg in soils/sediments along the former Plainwell Mill banks to a target concentration of 4 mg/kg
- Reconstruct bank, as needed to minimize future release of PCBs
- Reconfigure bank to limit upland cutbacks into former Plainwell Mill property and place erosion controls to provide comparable stability to pre-excavation conditions

To achieve the excavation objectives stated above, physical and analytical data from previous investigations performed on sediments, bank soils and floodplain soils were reviewed to identify and delineate specific areas of sediment and soil to be targeted as part of this Emergency Action The design approach to the Emergency Action is presented in a draft final Plainwell Mill Banks Emergency Action Design Report (RMT, 2007c) Site preparation work is scheduled to begin late September 2007 with construction to follow in early October The 2 600 linear feet of bank length has been divided into four zones based upon physical conditions and estimated quantity of visual residuals targeted for excavation These construction zones will facilitate construction by providing an opportunity to refine the construction approach and schedule between each zone

2 3 PREDESIGN INVESTIGATIONS FOR THE REMEDIAL DESIGN FOR THE 12TH STREET LANDFILL (OPERABLE UNIT NO 4)

The 12th Street Landfill, composed primarily of the 6 5-acre closed landfill and the four areas outside the landfill where PCB-contaminated residual material has been observed, is Operable Unit No 4 (OU 4) of the Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site (Kalamazoo River Superfund Site) The landfill is situated with 17 acres of wetlands on an approximately 24-acre parcel Additional portions of OU-4 that are located outside the landfill property include the woodland area owned by the State of Michigan (State) under the management of the Michigan Department of Natural

Resources (MDNR) the asphalt plant operation adjacent to the landfill and the former powerhouse discharge channel Contamination in the former powerhouse discharge channel was addressed as part of Emergency Actions implemented in 2007

Paper residuals from the former Plainwell Mill (mill), located in Plainwell Michigan were disposed in the 12th Street Landfill during the period from approximately 1955 to 1983 The landfill reportedly also accepted solid waste from the mill during part of its period of active operation A number of investigations have been performed at the site The investigations have confirmed the nature of the material in the landfill and have shown that paper residuals are present in certain areas outside of the landfill (*i e* in the wetlands to the north/northwest, the asphalt plant property, and the State property) Some of the residuals/native soil beyond the toe of the landfill (*i e* , outside the footprint of the landfill) may contain PCBs at concentrations exceeding State of Michigan or Kalamazoo River Superfund Site-specific ecological risk-based criteria

A ROD for OU-4 was issued on September 28 2001 The major components of the selected remedy include the following (1) the excavation and relocation into the landfill of contaminated residuals currently in the woodland, wetlands, and adjacent property, and the residuals in the former powerhouse discharge channel that are contiguous with the eastern side of the landfill followed by the construction of a containment system, (2) the excavation and relocation into the landfill of the east side of the landfill along the former powerhouse discharge channel to create a buffer zone sufficient to insure no hydraulic connection between the wastes within the landfill containment system and the Kalamazoo River or the former powerhouse discharge channel (3) the restoration of areas excavated cleared and grubbed or otherwise affected by the remedial action (4) the construction of a side wall containment system around the outside of the landfill, (5) the construction of a cover (cap) over the landfill, (6) the installation of an appropriate groundwater monitoring network and the performance of long-term groundwater monitoring, (7) the performance of short-term surface water monitoring (8) the placement of deed restrictions, (9) the construction of a fence, permanent markers and warning signs, (10) the investigation of the need for a leachate collection system and, if deemed necessary the construction of a leachate collection system, and (11) the implementation of long-term maintenance and post-closure care '

In January 2005 Weyerhaeuser negotiated a CD with the U S EPA (Civil Action No 1 05 CV0003) for the design and implementation of certain response actions at Operable Unit #4 and the Plainwell, Inc Mill These actions include the RD/RA activities for the 12th Street Landfill This revision of the Multi-Area QAPP has been prepared in fulfillment of the requirements for an RD Workplan for the 12th Street Landfill that are contained in the CD and the SOW

The RD Workplan for the 12th Street Landfill includes a number of predesign investigations some of which will involve field data collection and visual observations Field data collection activities will include visual information obtained by the advancement of test pits visual information obtained by the advancement of Geoprobe® borings, and gas concentration measurements (methane, carbon dioxide, and oxygen) in existing monitoring wells and in the Geoprobe® borings advanced as part of the predesign investigation

The field investigations will involve 1) a determination of the extent of visible paper residuals beyond the landfill footprint, 2) the collection of data to support the grading design for the final landfill cover, and 3) the collection of data for use in the design of a landfill gas venting system Sufficient information is available from previous investigations to evaluate the potential need for a leachate collection system No additional field information is needed to support this objective

2 3 1 EXTENT OF PAPER RESIDUALS BEYOND LANDFILL FOOTPRINT

The objectives of this investigation include the following

Wetland

- To confirm the approximate areal extent of visible paper residuals beyond the toe of the landfill as delineated based on the results from previous investigations
- To assess the degree of difficulty in distinguishing the visible paper residuals from the native soil
- To evaluate potential constructability issues associated with working in the wetland north of the landfill

Asphalt Plant/State Properties

- To delineate the areal extent, and to better estimate the depth of visible paper residuals on the asphalt plant property to the southwest and on the State property to the southeast in order to support discussions with owners of these adjacent properties concerning access for conducting the remedial actions on the properties required by the ROD

The general scope of the predesign investigation includes the following activities

Wetland

- Excavate approximately three test pits at the locations depicted on Figure 2-2 The test pits are anticipated to be approximately 10 to 15 feet long (perpendicular to the edge of the landfill) and approximately 2 to 4 feet wide The test pits will be excavated to a maximum depth of 3 feet if no paper residuals are visually apparent, or to the bottom of visually-identifiable residuals

Asphalt Plant/State Properties

- Excavate approximately three test pits on the asphalt plant property, and approximately four test pits on the State property at the locations depicted on Figure 2-2 The test pits are anticipated to be approximately 10 to 15 feet long (perpendicular to the edge of the landfill) and approximately 2 to 4 feet wide The test pits will be excavated to a maximum depth of 3 feet if no paper residuals are visually apparent or to the bottom of visually-identifiable residuals

  In the event that in-field conditions limit the use of test pit excavating equipment (*e g*, a backhoe), other tools, such as hand augers or shovels, may be used instead In such instances, the U S EPA project manager, or designated alternate, will be contacted to discuss the situation and to agree on a course of action In addition, Weyerhaeuser will conduct a kick-off meeting with the U S EPA and its field representative(s) at the outset of the predesign field investigation During this meeting the schedule for conducting the predesign field activities and the process for obtaining U S EPA approval of field modifications will be reviewed

2 3 2 GRADING DESIGN

The objective of this investigation is the following

- To better estimate the depth of the paper residuals along the property boundaries with 12th Street the asphalt plant to the southwest, and with the State property to the southeast in order to reduce uncertainties in designing the final landfill grades

The general scope of this investigation is the following

- Advance approximately nine Geoprobe® borings into the 12th Street Landfill at locations where fill material is believed to extend beyond the property boundaries to the southwest and to the southeast (see locations on Figure 2-3) The borings will be advanced approximately 5 feet into the native soil underlying the fill, or to refusal
- Advance a minimum of two soil borings (RDB-10 and RDB 11) near the southern end of the landfill, as shown on Figure 2-3, to confirm the thickness of the fill in this area Advance the borings approximately 5 feet into the native soil underlying the fill or to refusal The locations of these borings may be adjusted in the field as necessary to avoid underground or aboveground utility lines Additional borings may be installed to the north of the initial borings as may be deemed useful by Weyerhaeuser in consultation with oversight agencies as needed for purposes of designing the landfill cover (*e g* if fill material is not encountered at a location where existing data indicate that fill is present)

2 3 3 LANDFILL GAS MANAGEMENT

The objective of this investigation is the following

- To collect readily accessible information about the subsurface landfill gas conditions at the 12th Street Landfill that may be useful in designing a passive gas venting system for the 12th Street Landfill

The general scope of this field investigation is the following

- Measure the concentrations of methane carbon dioxide and oxygen in the existing groundwater monitoring wells at the 12th Street Landfill that are screened in the vadose zone (MW-6A, MW-7A and MW-8A) and in the Geoprobe® boreholes used to estimate the depth of the paper residuals along the property boundaries (see locations on Figure 2-3) Pressures that may have developed within the groundwater monitoring wells caused by excess landfill gas (if present) will also be measured A passive gas venting system can be designed without the above information If these data cannot be readily obtained additional efforts will not be employed to collect the information

2 4 RI/FS AT THE PLAINWELL MILL (OPERABLE UNIT NO 7)

2 4 1 PHASE 2 OF ADDENDUM NO 1

In a letter to Weyerhaeuser dated February 19, 2008, the U S EPA requested additional work along the former Plainwell Mill banks in response to discovery of elevated concentrations of PCBs and oily soil encountered along the Plainwell Mill banks during the separate Plainwell Mill Banks Emergency Response activities On July 15 2008 a Draft Phase 2 Addendum No 1 to the Plainwell Mill RI/FS Work Plan was prepared and provided to U S EPA for review The U S EPA provided technical review comments on the Draft Phase 2 Addendum No 1 in a letter dated July 31 2008 Subsequently, Weyerhaeuser provided response to comments and a redlined version of the Work Plan Addendum in a letter dated August 8, 2008 The Phase 2 of Addendum No 1 Work Plan has been designed to meet the following objectives

1 Identify Source Identify, as much as possible a likely cause of the oily sheen observed near the former transformer pad with focus on the possible presence of NAPL

2 Determine Relationships Determine if there is a relationship between the oily material near the transformer pad and the elevated PCB concentrations found at PM-SD-041 PEX-1 and PEX 2 (Figure 2)

3 Assess NAPL Determine whether NAPL if present is entering the Kalamazoo River

4 Define Nature of Contamination Determine if the oily material present in soils and fill near the transformer pad and at locations PM SD 041, PEX-1 and PEX 2 contain petroleum products and/or PCBs

5 Develop Next Steps Determine immediate actions needed and how the next phase of investigation should be integrated with other RI activities

Due to the nature of the investigate areas likely to contain fill material and or construction debris, test pits have been selected as the best method for successful site characterization Test pits will be advanced to either native soils or the water table using an excavator taking care to minimize site disturbances to the extent practical Additional details and the rationale for the proposed test pit investigation are presented in the Phase 2 of Addendum No 1 Work Plan and the associated QAPP Worksheet #10-4

2 4 2 PLAINWELL MILL RI/FS – PHASE I INITIAL GROUNDWATER ASSESSMENT

The Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment includes a collection of shallow groundwater samples to assess the possible presence of floating product and to quantify the concentrations of constituents in shallow groundwater that may have been contributed by suspected or known contamination present on site The Plainwell Mill is located at 200 Allegan Street in Plainwell Michigan The limited existing groundwater data, the generally permeable subsurface sands present along the Kalamazoo River, the site history, and the size and configuration of the Plainwell Mill property make a phased groundwater investigation especially useful for focusing future data collection activities needed to meet the overall objectives of the required RI/FS

The specific objectives for the Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment are

- To determine if free product is present on the groundwater table at the monitoring well locations
- To evaluate shallow groundwater quality across the Plainwell Mill property
- To assess shallow site-specific hydro-geologic characteristics that will be used to refine the current site conceptual model

- To determine the potential usability of past site data in the determination of the nature and extent of contamination present on the Plainwell Mill
- To identify data gaps that need to be addressed during Phase II investigations of soil and groundwater

Groundwater sampled from each location will be analyzed for volatile organic compounds (VOCs) polycyclic aromatic hydrocarbons (PAHs), Resource Conservation and Recovery Act (RCRA) metals, and PCBs As a frame of reference concentrations of measured constituents will be compared to applicable Michigan standards

The results of this phase of the RI will also be used to help assess the potential usefulness of groundwater results from previous environmental assessments conducted on the site, better define site conditions, and then allow identification of data gaps The identified data gaps will then be addressed during the Phase 2 soil and groundwater sampling activities expected for this site Additional details and the rationale for the phased groundwater assessment are presented in the Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment Work Plan and the associated QAPP Worksheet #10-4

2 4 3 PLAINWELL MILL PHASE II RI WORK PLAN

Weyerhaeuser provided the U S EPA with a Phase II RI Work Plan for the Plainwell Mill on September 23 2009 A formal notification from the U S EPA to proceed with implementation of the Work Plan has not been received yet

The Phase II RI Work Plan investigation was developed to meet the following objectives

- Perform a supplemental groundwater investigation developed based on the results of the Phase I RI groundwater investigation to further evaluate the nature and extent of impacts to groundwater and their potential sources,
- Further assess shallow site-specific hydrogeologic characteristics and interconnections with the Kalamazoo River, and
- Perform soil investigations in the former wastewater sludge and dewatering lagoon and aeration basin area the area of the mill buildings, and the north central portion of the Plainwell Mill to adequately characterize the nature and

extent of impacts to soil in the unsaturated zone that may have occurred due to historical operations

To satisfy the needs for a comprehensive soil characterization program to fill the data gap and confirm the historical exceedances at Plainwell Mill three soil sampling programs have been developed based on the historical operations at the Site and available information for the purpose of proceeding with the proposed Phase II RI Work Plan sampling activities at the Plainwell Mill These programs will be referred to during the descriptions of scope of investigatory activities at the Site

Upon advancement of soil borings, soil cores will be examined for presence of visual and/or olfactory evidence of impact, and will be screened across their entire length using a photoionization detector (PID) to determine relative concentrations of undifferentiated volatile organic vapors The soil samples then will be collected by employing one of the following sampling programs based on the historical operations and/or information

- <u>Sampling Program 1</u>

  - One biased soil sample will be collected at the layer considered to be fill material (based on field observations) from 2 to 10 feet bgs If no visual and olfactory evidence of impacts and/or elevated PID readings are recorded, one soil sample will be collected from 0 to 2 feet above the interface of the fill and native material within the vadose zone,
  - One soil sample will be collected from 0 to 2 feet below the observed impact If no impact is observed the soil sample will be collected from 0 to 2 feet below the interface of the fill/ native material within the vadose zone, and
  - One soil sample will be collected at the vadose zone from 0 to 2 feet above the saturated zone

- <u>Sampling Program 2</u>

  - From soil borings exhibiting no evidence of impact, a discrete soil sample will be collected from 0 to 2 feet below the interface of the vadose and saturated zone If impact is noted one soil sample will be collected within 2 to 10 feet bgs and a

third sample will be collected from 0 to 2 feet above the interface of vadose and saturated zone

- Sampling Program 3

  - One surficial soil sample will be collected,
  - One biased soil sample will be collected from the fill material which is expected to encounter approximately at depths of 2 to 10 feet bgs Soil borings not exhibiting any evidence of impact will be sampled at 0 to 2 feet above the interface of fill/native material within vadose zone
  - One soil sample will be collected from 0 to 2 feet below the observed contamination If no evidence of impact is observed the soil sample will be collected from 0 to 2 feet below the interface of fill/native material within vadose zone and
  - One soil sample will be collected at vadose zone from 0 to 2 feet above the saturated zone

To facilitate the evaluation of the historical information Plainwell Mill has been divided into three areas based on their locations and noted historical environmental impacts The three areas are the former wastewater sludge dewatering lagoons and aeration basin (Area 1) mill building area (Area 2) and north central portion area of the Plainwell Mill (Area 3) Based on the review of the historical documentations, the following general scope of investigation has been developed to determine the potential impacts associated with historical activities and provide a complete assessment of the Plainwell Mill

- Area 1

Soil investigation and groundwater monitoring locations are depicted on Figure 2-2

Soil Investigation

- Investigation of the identified lagoon areas is proposed to confirm the depth and extent of potential contamination Installation of two soil borings one at each of the assumed peripheral ends of the former lagoons is proposed The location of the deep soil borings would be based on field identification to assess physical constraints and previous investigations Soil sampling will be conducted as per Sampling Program 1,

- Confirmation of exceedances noted during historical investigations and further delineation of soil chemistry from across the lagoon area as needed to meet the objectives of the RI Sampling will be focused on the 0 to 1 foot bgs interval to determine any direct exposure hazards to the public in relation to potential construction activities relating to the redevelopment of the Site
- Investigation of any potential impacts associated with the aeration basin as per Sampling Program 1,
- Investigation of any potential impacts in the areas adjacent to the lagoon and aeration basin to confirm the extent of the lagoons, any impacts associated with the surrounding soils resulting from migration of contaminants toward the Kalamazoo River, and determine historical morphing of the lagoon areas as per Sampling Program 1,
- Based on review of historical information the wooded area has remained unchanged throughout mill expansions An inspection of this area will occur prior to final placement of the borehole locations however the proposed locations would provide the appropriate data for initial characterization of this area Investigation of the wooded area southwest of the lagoon area to determine potential impact as per Sampling Program 2 Collection of one surficial soil sample will occur where impact is noted to be the greatest after field screening, and
- Collection of five samples to determine the soil physical properties for risk assessment purposes

<u>Groundwater investigation</u>

- Installation of one monitoring well (MW-13) screened within the paper waste to determine contaminate concentrations of the waste for comparison to the Site s analytical data,
- Re-installation of SGWB-2 (MW-14) located south west of the lagoon areas to characterize groundwater flow direction through this area and provide an alternate background monitoring well location for the lagoon area,
- Installation of a monitoring well north of the former secondary clarifier (MW 15) to determine any potential groundwater impacts related to prior discharges
- Soil sampling during installation of the new monitoring wells to characterize potential soil impacts in these areas

- Completion of VAS at location MW-13 within Lagoon J This area was selected to characterize the groundwater above within and below the residual paper waste location in this former lagoon area As indicated in historical borehole logs residual paper waste has been noted Further this location will provide information related to the depth of potential confining layers within the native soil beneath the paper waste, and
- Sampling of current monitoring wells (i e , MW 8, MW-9 MW-10, MW 11 and MW-12) and the three new monitoring wells (i e MW-13, MW 14 and MW-15) to determine and confirm groundwater impacts

- Area 2

Soil investigation and groundwater monitoring locations are depicted on Figure 2-3

<u>Soil Investigation</u>

- Confirmation and vertical delineation of potential contamination in the area of TP-17 and TP 18 surrounding the historical transformer pad located in the north east portion of the Site adjacent to the Kalamazoo River Sampling will be conducted as per Sampling Program 1 Collection of one surface sample will be completed in this area,
- Visual inspection of outflow points identified during previous investigations along the Kalamazoo River to ensure capping was conducted properly and no further issues pertain to these outflows Surface sampling may be conducted if any visual evidence of impact is noted
- Visual inspection of the surface soils surrounding the building to determine if any staining is present in relation to historical Site activities Surface soil sampling may be conducted if necessary
- Installation of one soil boring (MW-16) adjacent to the mill race to determine soil conditions adjacent to the mill building Samples will be collected as per Sampling Program 2,
- Installation of one soil boring (i e MW-17) in the southern corner of the parking lot area adjacent to the mill race for visual inspection A sample may be collected depending on field screening observations Samples will be collected as per Sampling Program 2
- Completion of two test pits within the undeveloped south parking lot and former background location BK5 to confirm the presence of fill below the parking lot areas and determine impacts associated with historical activities

Sampling will be conducted as per Sampling Program 2 along with the collection of one surface sample and

- Collection of samples to determine the soil physical properties for risk assessment purposes

Groundwater Investigation

- Installation of a monitoring well (i e , MW-16) adjacent to the mill building near the end of the mill race to further define the groundwater flow patterns at this area,
- Installation of one monitoring well (i e MW-17) in the southeast portion of the Site [near the staff gauge (i e , SG-1) located on the southern portion of the mill race] to determine influence of the mill race on the water levels at the southern property boundary,
- Although the two proposed monitoring wells will be sampled for chemical analysis the primary objective of these two locations is to further understand the hydraulic interaction of the mill race and groundwater
- VAS will occur adjacent to MW 4 This location is within the proximity of the Kalamazoo River and downgradient of the Mill Buildings Historical impacts have been noted at this location, therefore sampling will determine the depth of impact within this area and identify potential confining layers along the Kalamazoo River, and
- Collection of groundwater samples from previously installed monitoring wells (i e MW-1, MW-2 MW-3, MW-4 and MW-5) and the newly installed monitoring wells (i e , MW-16 and MW 17) to confirm the groundwater chemistry at the Site

Surface Water Investigation

Sampling within the Mill Race and the Kalamazoo River will be conducted to collect analytical data necessary for use of the Part 201 GSI screening criteria (i e , collection of hardness data) Sampling will also be conducted for low-level mercury, and methyl mercury to determine levels within the two adjacent water bodies for completion of the RI report Further, surface water levels will be measured to further understand the hydrogeologic conditions on Site

- Area 3

Soil investigation and groundwater monitoring locations are depicted on Figure 2 4

Soil investigation

- Carry out test pitting at seven locations within the undeveloped areas to confirm the presence of fill materials beneath the parking lot areas
- Advancement of three soil borings (i e , SB-301 SB-302 and SB-321) in the northern portion of the Area 3 will confirm the historical exceedances (i e DG3 DG4 and SGWB-10) observed at this portion of the Site Sampling at this location will follow Sampling Program 1
- Advancement of eight test pits (i e TP-308 through TP-315) will be excavated to depths of approximately 10 feet bgs to further identify the potential subsurface coal contamination within this area, to determine the location/depth of potentially contaminated soils and to confirm soil quality Soil sampling will be conducted as per Sampling Program 2,
- Advancement of five soil borings (i e SB 303 through SB-307) at the proximity of No 6 Fuel Tank Area to characterize any potential sources of impact Soil sampling will be conducted as per soil sampling program 3 which includes surface soil sampling based on field screening at each location, and
- Advancement of five soil borings (i e , SB-308 through SB-312) around the perimeter of the former Coal Storage Tunnel is proposed to characterize any potential sources of contamination around the fuel oil lines and to determine if potential soil impacts at depths below the bottom of the tunnel based on the results of the investigation during Phase I of the RI Soil sampling will be conducted as pre sampling program 2

Groundwater Investigation

- Re installation of SGWB-10 to confirm groundwater exceedances previously noted (i e MW-18)
- Collection of groundwater samples from existing monitoring wells (i e MW-6 and MW-7) and the new monitoring well (i e , MW-18) as part of Site wide groundwater sampling program to confirm the groundwater chemistry at the Site and

- Installation of one monitoring well (i e MW 19) to replace SGWA 5 will confirm previous groundwater impacts noted at No 6 Fuel Tank Area

Collected soil samples will be analyzed for Target Compound List (TCL) VOCs, TCL SVOCs, PCBs, Target Analyte List (TAL) metals as defined in this QAPP, Synthetic Precipitation Leaching Procedure (SPLP) metals and general chemistry parameters Collected groundwater from monitoring locations will be analyzed for TCL VOCs, TCL SVOCs, PCBs, and TAL inorganics In addition two surface water samples will be collected and analyzed for low level mercury, methyl mercury and hardness The results of these sampling activities will be used to demonstrate compliance with the Michigan Part 201 Generic Residential Cleanup Criteria (GRCC) pursuant to the MDEQ s Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria (STM, MDEQ, 2002)

2 5 REMEDIAL ACTION WORK PLAN AT 12TH STREET LANDFILL (OPERABLE UNIT NO 4)

The scope of the RA for the 12th Street Landfill includes excavation of paper residuals present outside the footprint of the landfill (on adjacent properties) landfill grading the construction of a landfill cover and erosion protection measures, and surface water management landfill gas management, construction of access road, abandonment of existing groundwater monitoring wells, installation of groundwater monitoring wells, and various environmental monitoring activities

2 5 1 EXCAVATION ACTIVITIES

The areal limits of visible paper residuals outside the footprint of the landfill on the MDNR property, the asphalt plant property and in the wetlands were previously delineated based on information obtained by Geraghty and Miller and the U S EPA in 1994 and 2003, respectively (G&M 1994b and U S EPA 2004), and have been refined based on the findings of the predesign investigation performed by Weyerhaeuser in 2008 Sufficient information is available from previous investigations to implement the excavation activities Upon completion of the excavation activities on the MDNR property and the asphalt plant property to the visual extent of the distinguishable paper residuals, samples of the native soil underlying the excavated paper residuals at the base

of the excavation will be collected and analyzed to confirm the adequacy of the excavation activities Collected soil samples will be analyzed for PCBs In addition samples collected from asphalt plant property will be analyzed for VOCs

This verification sampling will be used to demonstrate completion with the Michigan Part 201 GRCC pursuant to the MDEQ s Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria (STM, MDEQ, 2002)

3 0 DOCUMENT OVERVIEW

This Multi Area QAPP has been developed in accordance with the UFP QAPP guidance (U S EPA 2005a), which is composed of a series of 37 worksheets, along with a series of attachments The worksheets provide information on project management project objectives, measurement and data acquisition, project assessment and oversight, and data review The attachments include chain-of-custody records, laboratory certifications laboratory quality assurance plans, and laboratory standard operating procedures (SOPs) In accordance with the U S EPA guidance, cross referencing is utilized where applicable in order to streamline the document This includes providing references to planning documents that are companion documents to this Multi-Area QAPP

4 0 REFERENCES

Arcadis BBL 2007a Former Plainwell impoundment time critical removal action design report Kalamazoo River Study Group Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund Site February 2007

Arcadis BBL 2007b Multi-area quality assurance project plan (Rev 00) Kalamazoo River Study Group, Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund Site April 2007

BBL 1993 Remedial investigation/Feasibility study quality assurance project plan Kalamazoo River Study Group, Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site June 1993

CRA 2009 Multi-Area Field Sampling Plan, Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund site Revision 05, September 23 2009

CRA 2009 Phase II Remedial Investigation Work Plan Former Plainwell, Inc Mill Property, Plainwell Michigan Operable Unit No 7 of the Allied Paper Inc /Portage Creek/Kalamazoo River Superfund site Version 3 September 23, 2009

CRA, 2009 Remedial Action Work Plan for 12th Street Landfill Otsego Township Michigan Operable Unit No 4 of the Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund site Revision 2 June 17 2009

G&M 1994 Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund site remedial investigation/feasibility study, Technical Memorandum 8 12th Street Landfill Operable Unit Plainwell Michigan May 31, 1994

RMT, Inc 2006 Draft quality assurance project plan for the remedial investigation/feasibility study (Rev 0) Plainwell Mill, Plainwell, Michigan September 2006

RMT Inc 2007a Bathymetry and visual sediment assessment data quality objectives and work scope technical memorandum Emergency response action, 12th Street Landfill (OU 4), Plainwell Michigan June 6, 2007

RMT, Inc 2007b Geotechnical investigation data quality objectives and workscope technical memorandum Emergency response action 12th Street Landfill (OU-4), Plainwell, Michigan May 11, 2007

RMT Inc 2007c Plainwell Mill banks emergency action design report September 2007

USDA 2004 Wells R E J Langendoen, and A Simon Numerical simulation of sediment loads and channel changes along the Kalamazoo River between Plainwell and Otsego City Michigan USDA-ARS National Sedimentation Laboratory Research Report No 44 46 pp

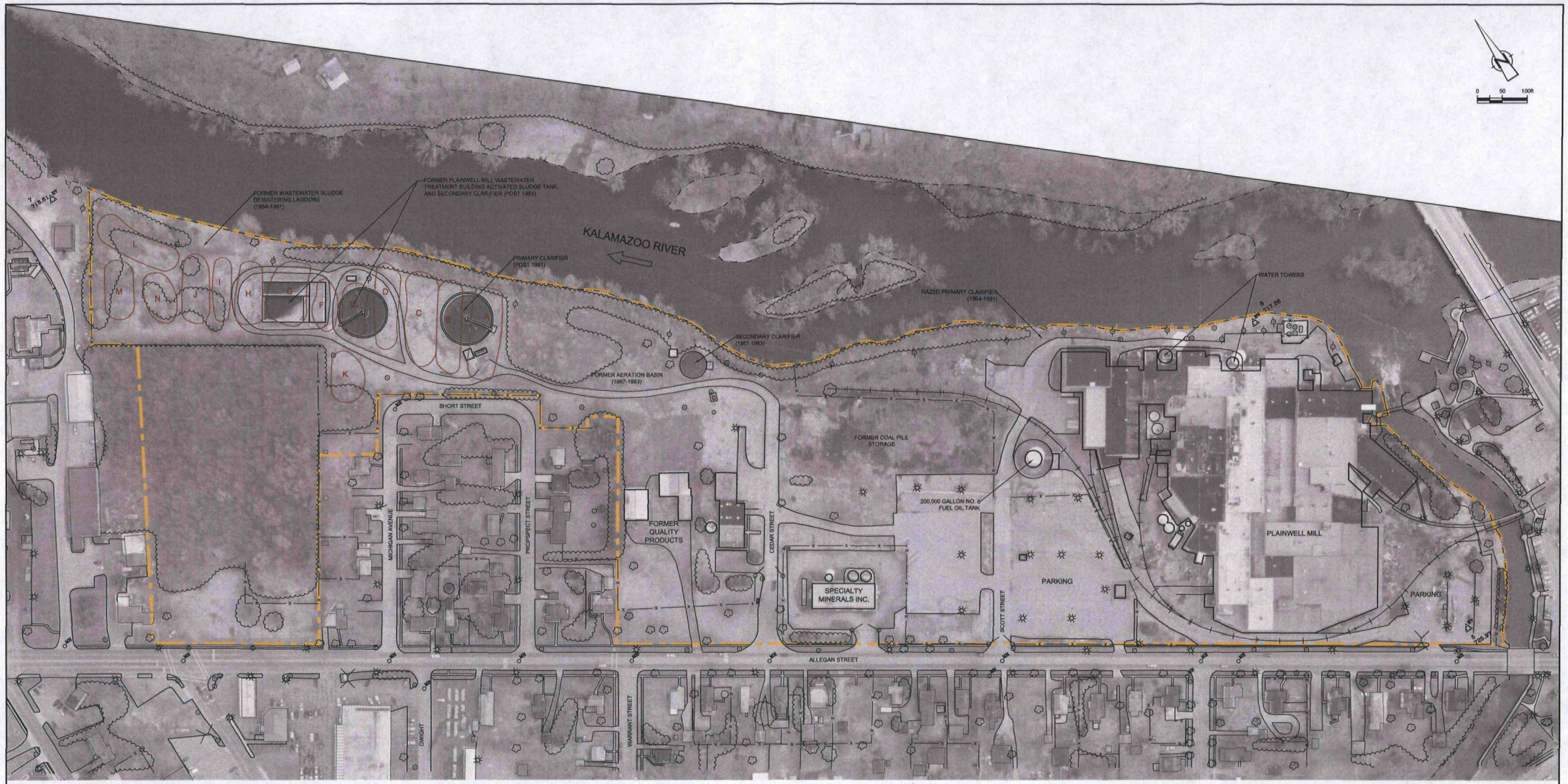
USGS 2004 Syed, A U J P Bennett and C M Rachol A pre-dam-removal assessment of sediment transport for four dams on the Kalamazoo River between Plainwell and Allegan, Michigan U S Geological Survey Scientific Investigations Report 2004-5178 41 p

U S EPA 1999 U S EPA contract laboratory program National functional guidelines for organic data review EPA 540/R-99/008 October 1999

U S EPA 2004 Final data summary report soil/sediment sampling results pre design sampling 12th Street Landfill Operable Unit #4, Allied Paper, Inc /Portage Creek/Kalamazoo River Site, Plainwell, Michigan July 2004

U S EPA 2005a Uniform federal policy for quality assurance project plans Evaluating, assessing, and documenting environmental data collection and use programs Part 1 UFP-QAPP Manual (Version 1) Pub Nos , EPA EPA-505 B 04 900A DoD DTIC ADA 427785 March 2005

U S EPA 2005b Uniform federal policy for quality assurance project plans Part 2B quality assurance/quality control compendium minimum QA/QC activities (Version 1) Pub Nos , EPA EPA 505-B 04-900B DoD DTIC ADA 426957 March 2005



LEGEND

SITE BOUNDARY	UTILITY POLE
SHORELINE	LIGHT STANDARD
FORMER WASTEWATER SLUDGE DEWATERING LAGOONS	MANHOLE
FENCELINE	SIGN
RAILWAY	SURVEY BENCHMARK
VEGETATION	

SCALE VERIFICATION: THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

No	Revision	Date	Initial

Approved

SITE PLAN

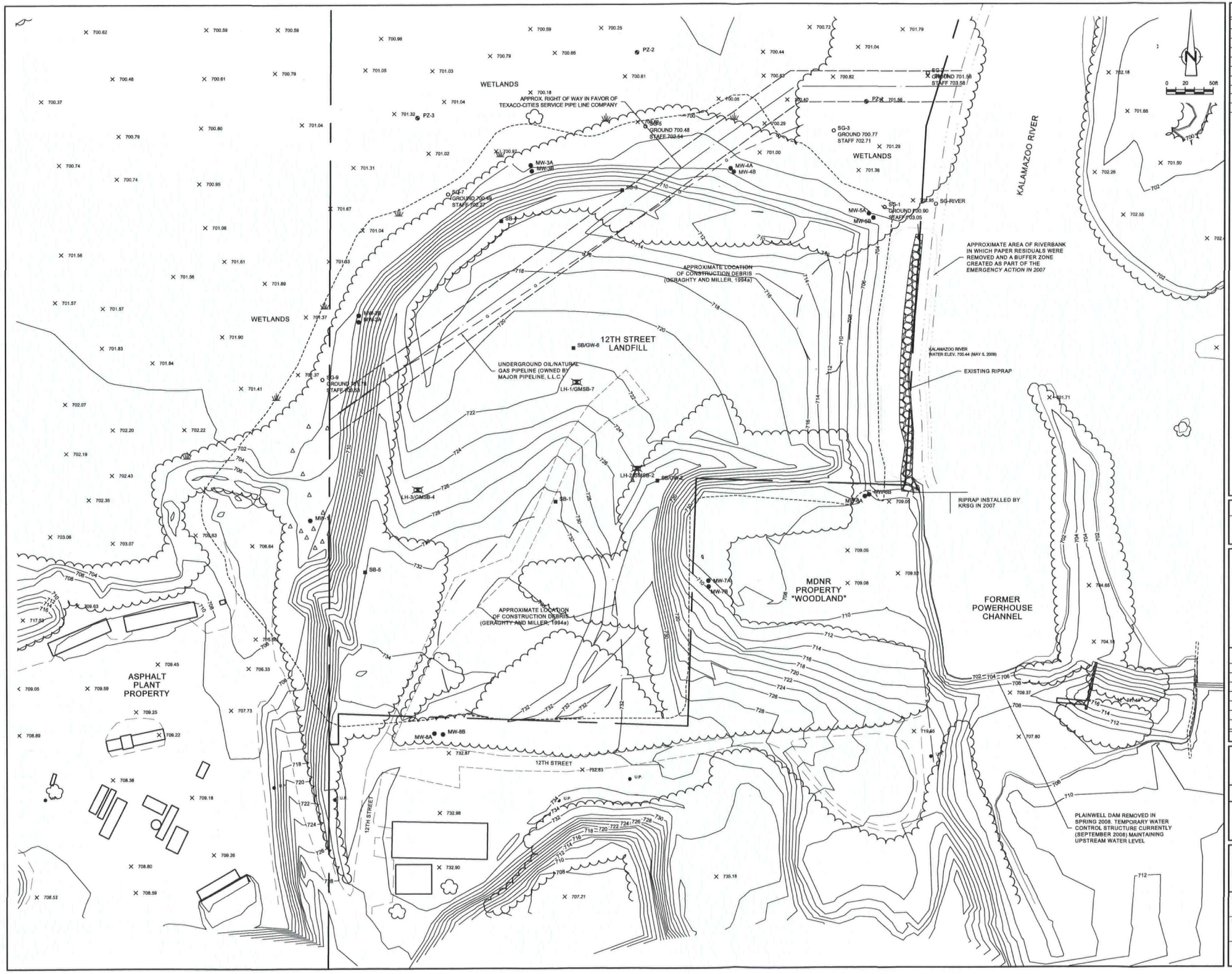
MULTI-AREA QUALITY ASSURANCE PLAN

FORMER PLAINWELL, INC MILL PROPERTY
PLAINWELL, MICHIGAN

CONESTOGA-ROVERS & ASSOCIATES

Source Reference:			Date: SEPTEMBER 2009
Project Manager: G. CARLI	Reviewed By: E. STAHL	Designed By:	Drawn By: C. JACOBI
Scale: 1:100	Project No: 056394-04	Report No: 003	Drawing No: FIGURE 2-4

056394-04(003)GN-SC003 SEP 23/2009



Nº	Revision	Date	Initial
1	UPDATED FOR SECOND EPA SUBMISSION	JUNE 15, 2009	C.R.H.

LEGEND

- APPROXIMATE PROPERTY BOUNDARY
- EXISTING PAVED ROAD
- EXISTING UNPAVED ROAD
- EXISTING FENCE
- EXISTING BUILDING
- EXISTING GROUND CONTOUR ELEVATION
- EXISTING SPOT ELEVATION
- EXISTING TREES AND/OR BRUSH
- EXISTING WET AREA AND WETLAND
- EXISTING EDGE OF WATER
- EXISTING LIMITS OF PAPER RESIDUALS
- APPROXIMATE LIMITS OF CONSTRUCTION DEBRIS
- MW-1 *EXISTING MONITORING WELL LOCATION*
- PZ-2 EXISTING PIEZOMETER LOCATION
- LH-1/GMSB-7 EXISTING LEACHATE HEAD WELL LOCATION
- SG-1 EXISTING STAFF GAUGE
- EXISTING VANE SHEAR TEST LOCATION
- SB-5 EXISTING INSPEC-SOL SOIL BORING LOCATION
- SB/GW-6 EXISTING INSPEC-SOL SOIL BORING LOCATION/GAS WELL

NOTES:

1. BOUNDARY AND TOPOGRAPHIC SURVEY COMPLETED BY PREIN & NEWHOFF ON MAY 19, 2009.
2. THE APPROXIMATE LIMITS OF VISIBLE PAPER RESIDUALS WERE DERIVED FROM THE ALLIED PAPER, INC./PORTAGE CREEK / KALAMAZOO RIVER SUPERFUND SITE REMEDIAL INVESTIGATION, TECHNICAL MEMORANDUM 9, (G & M 1994b) AND REVISED BASED ON THE U.S.EPA'S 2003 PREDESIGN INVESTIGATION (U.S. EPA, 2004), THE EMERGENCY ACTIONS PERFORMED ALONG THE RIVERBANK IN 2007 (RMT, 2008b), AND THE PREDESIGN INVESTIGATION CONDUCTED IN JUNE 2008 (COPIED IN APPENDIX A OF THIS REPORT).
3. THE OIL/NATURAL GAS PIPELINE IS CURRENTLY (SEPTEMBER 2008) INACTIVE. IT WAS BURIED IN NATIVE SOIL PRIOR TO DISPOSAL OF PAPER RESIDUALS IN THE LANDFILL. THIS PIPELINE IS BURIED BELOW GRADE.

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

Approved

DRAWING STATUS

Status	Date	Initial

12th STREET LANDFILL
Otsego Township, Michigan

MULTI-AREA QUALITY ASSURANCE PLAN

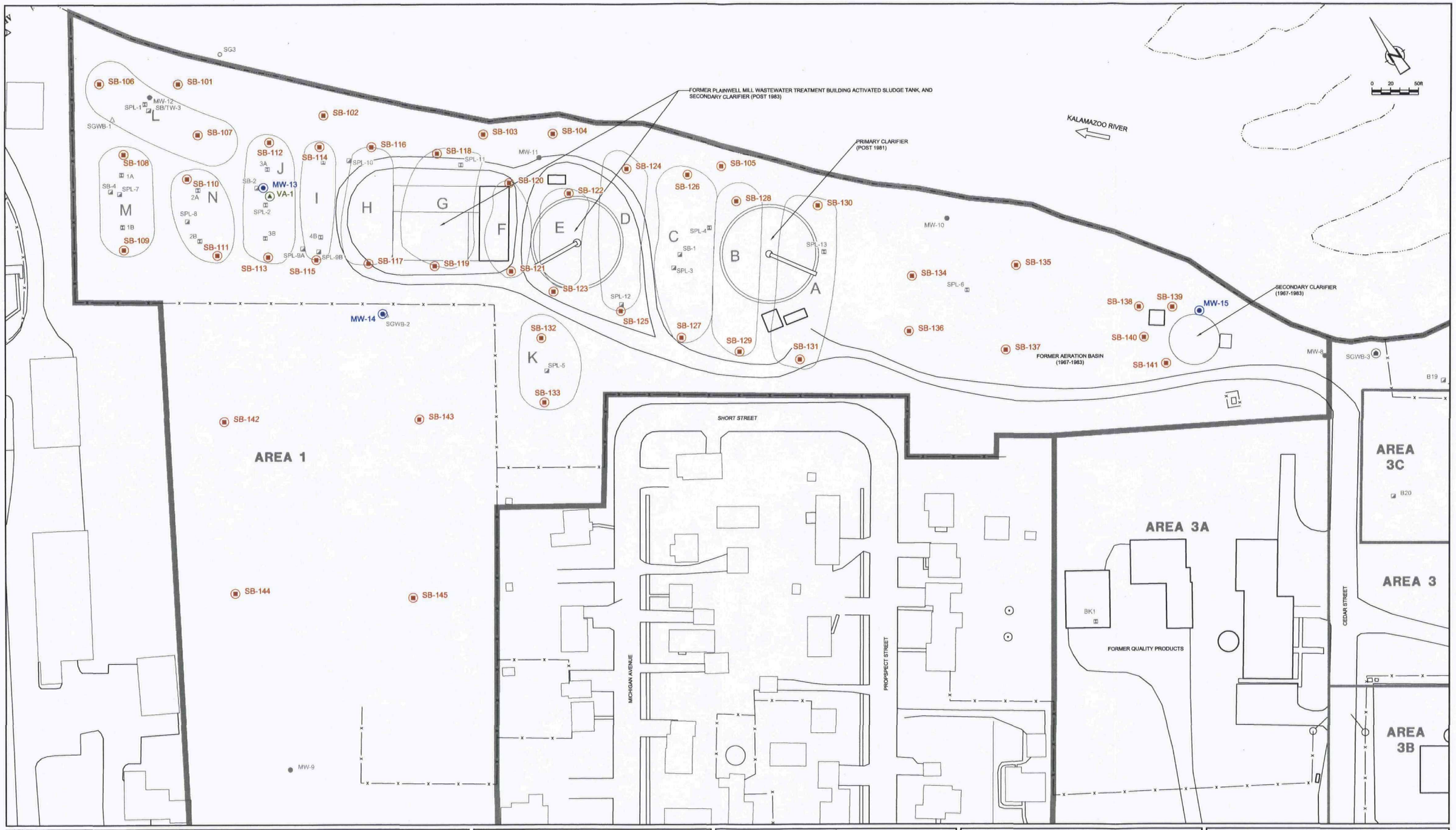
SITE LAYOUT

CONESTOGA-ROVERS & ASSOCIATES

Source Reference: BASE ADAPTED FROM PREVIOUS RMT DESIGN

Project Manager:	Reviewed By:	Date:	
G. CARLI	G. BOLOURANI	SEPTEMBER 2009	
Scale: 1" = 50'-0"	Project Nº: 056394-04	Report Nº: 003	Drawing Nº: 2-5

056394-04(003)GN-SC004 SEP 23/2009



LEGEND

- AREA BOUNDARY
- SHORELINE
- FORMER WASTEWATER SLUDGE DEWATERING LAGOONS
- FENCELINE
- VEGETATION
- PROPOSED MONITORING WELL LOCATION
- PROPOSED SOIL BORING LOCATION
- PROPOSED VERTICAL AQUIFER TESTING LOCATION
- PREVIOUS SOIL SAMPLE LOCATION
- PREVIOUS SOIL BORING LOCATION
- PREVIOUS MONITORING WELL LOCATION
- PREVIOUS TEMPORARY WELL LOCATION
- PREVIOUS GROUNDWATER SAMPLE LOCATION
- PREVIOUS STAFF GAUGE LOCATION (APPROXIMATE)

NOTE: LOCATIONS IN WOODED AREAS ARE APPROXIMATE, ACTUAL LOCATIONS TO BE DETERMINED IN THE FIELD.

SCALE VERIFICATION: THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

No	Revision	Date	Initial

Approved

AREA 1 PROPOSED PHASE II SAMPLE LOCATIONS

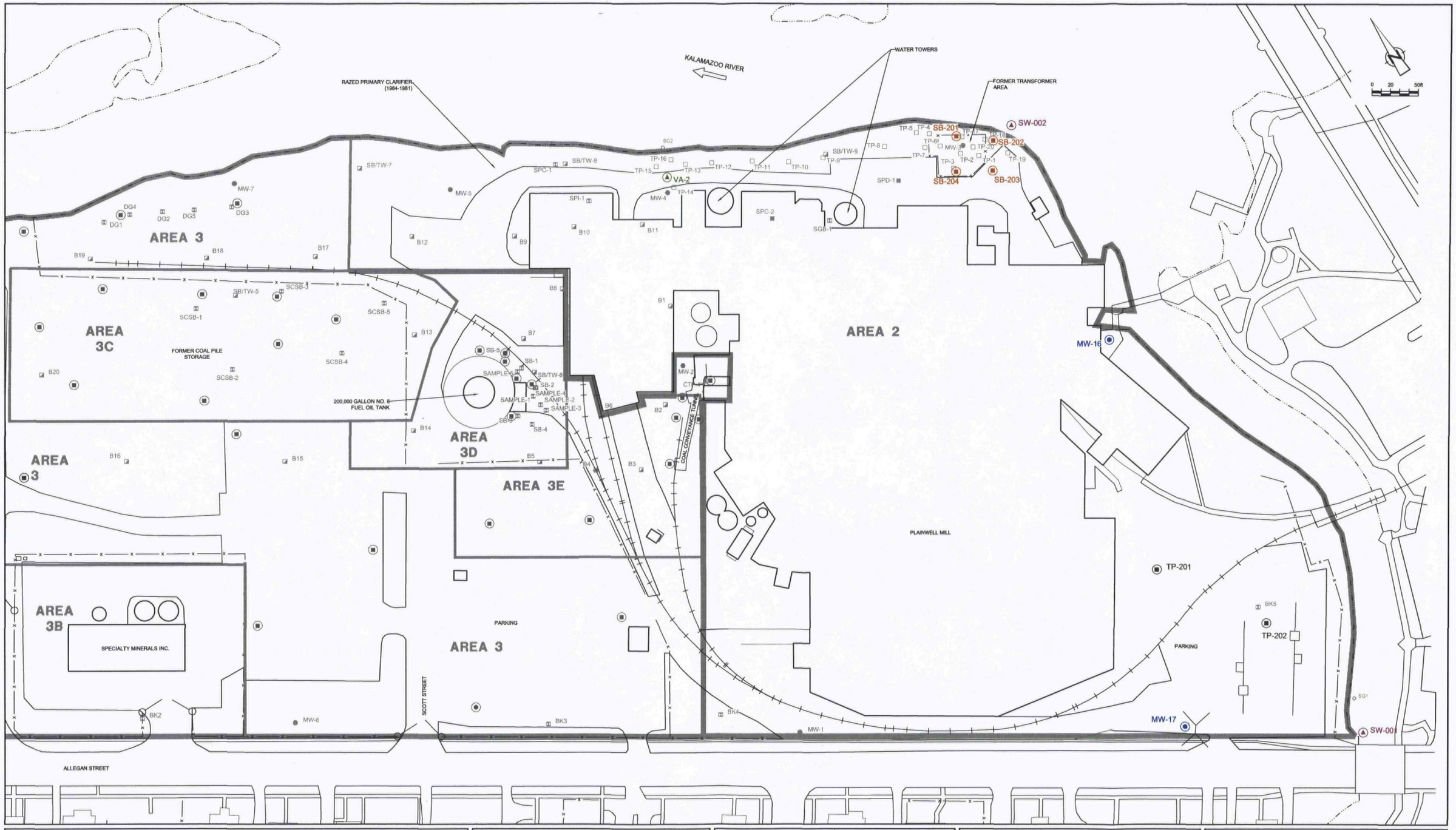
MULTI - AREA QUALITY ASSURANCE PROJECT PLAN

FORMER PLAINWELL, INC MILL PROPERTY
PLAINWELL, MICHIGAN

CONESTOGA-ROVERS & ASSOCIATES

Source Reference: RMT PROJ. 00-05121.03			Date: MAY 2009
Project Manager: G. CARLI	Reviewed By: E. STAHL	Designed By:	Drawn By: C. JACOBI
Scale: 1:100	Project No: 056394-04	Raport No: 003	Drawing No: FIGURE 2-6

056394-04(003)GN-SC006 SEP 22/2009



LEGEND

- AREA BOUNDARY
- SHORELINE
- RAILWAY
- FENCELINE
- VEGETATION
- PROPOSED MONITORING WELL LOCATION
- PROPOSED SOIL BORING LOCATION
- PROPOSED SURFACE WATER SAMPLE LOCATION
- PROPOSED TEST PIT LOCATION
- PROPOSED VERTICAL AQUIFER TESTING LOCATION
- PREVIOUS SOIL SAMPLE LOCATION
- PREVIOUS SOIL BORING LOCATION
- PREVIOUS TEST PIT
- PREVIOUS SEDIMENT SAMPLE LOCATION
- PREVIOUS GROUNDWATER MONITORING WELL LOCATION
- PREVIOUS GROUNDWATER SAMPLE LOCATION
- PREVIOUS STAFF GAUGE LOCATION (APPROXIMATE)

SCALE VERIFICATION: THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

No	Revision	Date	Initial

Approved

AREA 2 PROPOSED PHASE II SAMPLE LOCATIONS

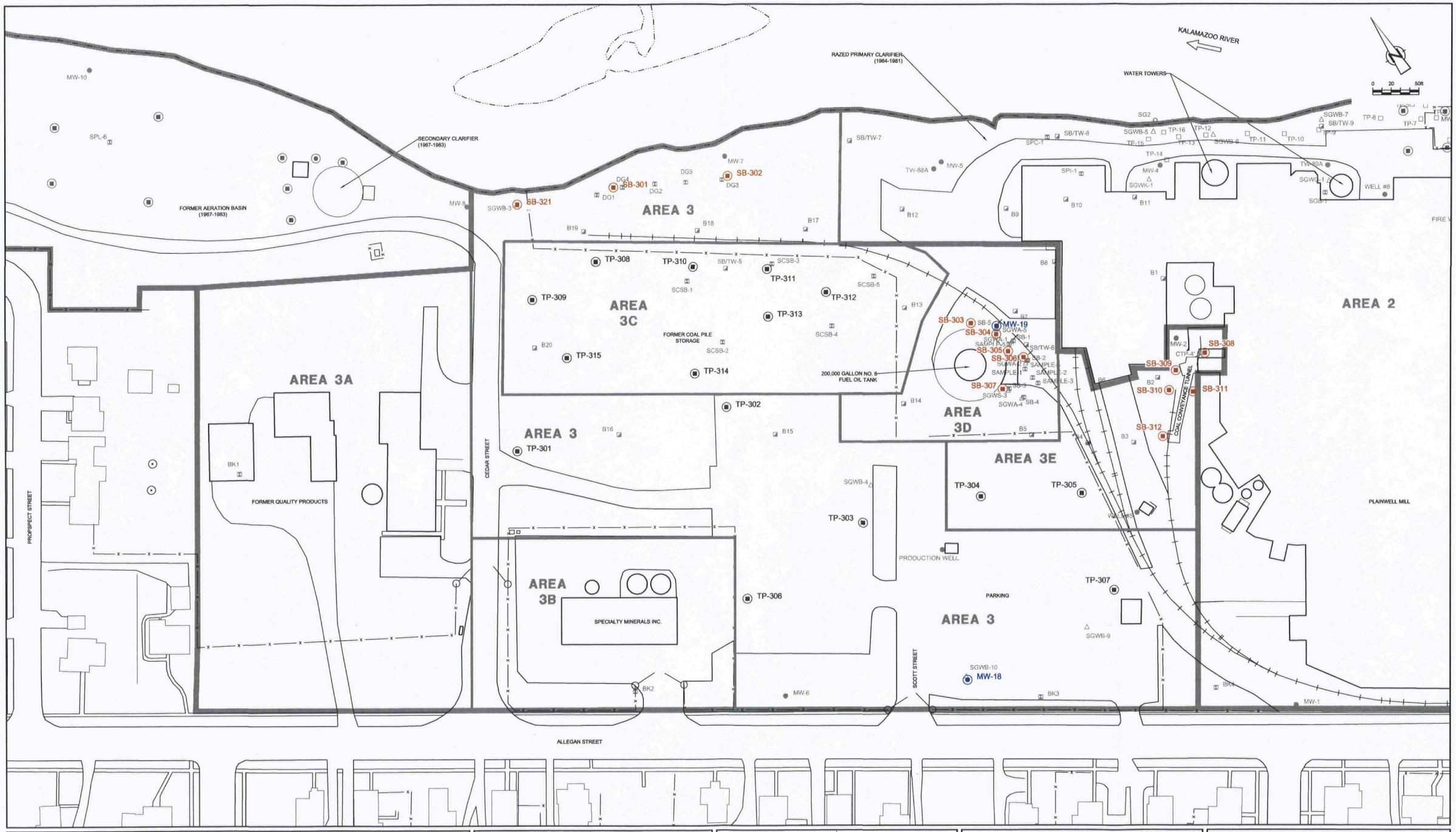
MULTI - AREA QUALITY ASSURANCE PROJECT PLAN

FORMER PLAINWELL, INC MILL PROPERTY
PLAINWELL, MICHIGAN

CONESTOGA-ROVERS & ASSOCIATES

Source Reference: RMT PROJ. 00-05121.03			Date: MAY 2009
Project Manager: G. CARLI	Reviewed By: E. STAHL	Designed By:	Drawn By: C. JACOBI
Scale: 1:100	Project No: 056394-04	Report No: 003	Drawing No: FIGURE 2-7

056394-04(003)GN-SC007 SEP 22/2009



LEGEND

- AREA BOUNDARY
- SHORELINE
- RAILWAY
- FENCELINE
- VEGETATION
- PROPOSED MONITORING WELL LOCATION
- PROPOSED SOIL BORING LOCATION
- PROPOSED TEST PIT LOCATION
- PREVIOUS SOIL SAMPLE LOCATION
- PREVIOUS SOIL BORING LOCATION
- PREVIOUS TEST PIT
- PREVIOUS SEDIMENT SAMPLE LOCATION
- PREVIOUS GROUNDWATER MONITORING WELL LOCATION
- PREVIOUS GROUNDWATER SAMPLE LOCATION
- PREVIOUS STAFF GAUGE LOCATION (APPROXIMATE)

SCALE VERIFICATION: THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

No	Revision	Date	Initial

Approved

AREA 3 PROPOSED PHASE II SAMPLE LOCATIONS

MULTI - AREA QUALITY ASSURANCE PROJECT PLAN

FORMER PLAINWELL, INC MILL PROPERTY
PLAINWELL, MICHIGAN

CONESTOGA-ROVERS & ASSOCIATES

Source Reference: RMT PROJ. 00-05121.03			Date: MAY 2009
Project Manager: G. CARLI	Reviewed By: E. STAHL	Designed By:	Drawn By: C. JACOBI
Scale: 1:100	Project No: 056394-04	Raport No: 003	Drawing No: FIGURE 2-8

056394-04(003)GN-SC005 SEP 22/2009

WORKSHEETS

QAPP Worksheet #1
Title and Approval Page

Site Name/Project Name	Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site
Site Location	Kalamazoo and Allegan Counties including (but not limited to) 3 miles of Portage Creek and the Kalamazoo River from the City of Kalamazoo to Lake Michigan ▪ Operable Unit No 4 12th Street Landfill ▪ Operable Unit No 7 Plainwell Mill
Document Title	Multi Area Quality Assurance Project Plan Weyerhaeuser Company
Lead Organization.	U S EPA Region 5
Preparer's Name and Organizational Affiliation.	Gregory A Carli, P E CRA
Preparer's Contact Information	261 Martindale Road Unit# 3 St Catharines ON L2W 1A2 gcarli@craworld com
Preparation Date (1) Revision 03 Addendum No 4 represents change in Project Coordinator from RMT to CRA and only includes worksheets relevant to CRA activities	Revision 00 June 2007 Revision 01 September 2007 (*i e* Addendum) Revision 02 February 2008 Revision 02, Addendum 2 September 2008 Revision 02, Addendum 3 November 2008 Revision 03 Addendum 4 June 2009
Investigative Organization s Project Manager For Investigative Activities at the Plainwell Mill (Operable Unit No 7)	Signature Gregory Carli, CRA
Investigative Organization s Project Manager For Investigative Activities at the 12th Street Landfill (Operable Unit No 4)	Signature Gregory Carli CRA
Investigative Organization s QA Officer	Signature Paul Wiseman CRA
Lead Organization s Program Manager for the 12th Street Landfill (Operable Unit No 4)	Signature Michael Berkoff U S EPA Region 5
Lead Organization s Program Manager for the Plainwell Mill (Operable Unit No 7)	Signature Sam Chummar, U.S EPA Region 5
Weyerhaeuser Analytical Testing Services (WATS) Laboratory Manager	Signature Dennis Catalano Weyerhaeuser
Columbia Analytical Services Inc (CAS) Laboratory Manager	Signature Jeff Christian CAS

QAPP Worksheet #1
Title and Approval Page

U S EPA Quality Assurance Reviewer	Signature U S EPA Region 5

Document Control Number 56394 (3) 001

QAPP Worksheet #2
Identifying Information

Site Name/Project Name	Allied Paper Inc./Portage Creek/Kalamazoo River Superfund Site
Site Location	Kalamazoo and Allegan Counties including (but not limited to) 3 miles of Portage Creek and the Kalamazoo River from the city of Kalamazoo to Lake Michigan ▪ Operable Unit No 4 12th Street Landfill ▪ Operable Unit No 7 Plainwell Mill
Site Number/Code	MID006007306
Operable Unit	Operable Units No 4 and 7
Contractor s Name	NA
Contractor s Number	NA
Contract Title	NA
Work Assignment Number	NA
Identify guidance used to prepare QAPP	Uniform Federal Policy for Quality Assurance Project Plans Manual VI (U S EPA 2005a)
Identify regulatory program	Comprehensive Environmental Response Compensation, and Liability Act (CERCLA)
Identify approval entity	U S EPA Region 5
Indicate whether the QAPP is a generic or a project-specific QAPP	This is a project specific Multi Area QAPP for Remedial Action implementation at the 12th Street Landfill (Operable Unit No 4) and the Remedial Investigation activities at the Plainwell Mill (Operable Unit No 7) This QAPP will be updated as required for future work at the 12th Street Landfill Site and Plainwell Mill.
List dates of scoping sessions that were held	Emergency Activities for the 12th Street Landfill May 8 2007 and June 6 2007 at U S EPA Region 5 offices in Chicago Illinois Emergency Activities for the Plainwell Mill Banks August 14 2007 Submittal of conceptual design approach and follow up discussions regarding U S EPA comments Predesign Investigations for the RD for the 12th Street Landfill December 7 2007 at U S EPA Region 5 offices in Chicago Illinois and on January 9 2008 via conference call

QAPP Worksheet #2
Identifying Information

List dates of scoping sessions that were held (Continued)	Work Plan preparation and comment discussion for Phase 2 of Addendum No 1 and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment July 16 2008 July 22 2008 via conference call Plainwell Mill RI Work Plan preparation and submittal of Phase II RI Work Plan, May 20 2009 and related follow up discussions on June 17 2009 12th Street Landfill Design medications as presented in CRA memorandum to U S EPA dated April 23 2009 Pre-Final Design Report Addendum No 1 (May 27 2009) and related conference calls on April 17 2009 and May 1 2009
List dates and titles of QAPP documents written for previous site work, if applicable	
Quality Assurance Project Plan, organization partners (stakeholders) and connection with lead organization	**(Site-Wide QAPP)** Blasland & Bouck Engineers P C 1993 Quality Assurance Project Plan June 1993 Prepared on behalf of the Kalamazoo River Study Group (KRSG) Approved by the U S EPA Region 5 and the Michigan Department of Natural Resources (MDNR) Other stakeholders included the Michigan Department of Environmental Quality (MDEQ) the United States Fish & Wildlife Service and the National Oceanic & Atmospheric Administration. **(Operable Unit No 7)** RMT 2006 Draft Quality Assurance Project Plan for the Remedial Investigation/Feasibility Study – Plainwell Mill September 2006 Prepared on behalf of Weyerhaeuser Company Project stakeholders include the MDEQ and the City of Plainwell **(Site-Wide QAPP)** RMT Rev 02 Addendum 3 2008 This Multi Area QAPP prepared on behalf of Weyerhaeuser and its representatives within the Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site Stakeholders include the U S EPA and the Michigan Department of Environmental Quality (MDEQ) with response pending **(Site-Wide QAPP)** CRA Rev 03 Addendum 4 2009 (current Addendum) This Multi Area QAPP prepared on behalf of Weyerhaeuser and its representatives within the Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site This document addresses activities associated with the Phase II RI Work Plan at the Plainwell Mill and the removal activities associated with the Remedial Action (RA) at the 12th Street Landfill Project stakeholders include the U S EPA and the Michigan Department of Environmental Quality (MDEQ) with response pending
List data users	Weyerhaeuser Company U S EPA Region 5

QAPP Worksheet #2
Identifying Information

Lead Organization s Program Manager	**Operable Unit No 4** Michael Berkoff U S EPA Region 5 Remedial Project Manager (RPM) **Operable Unit No 7** Sam Chummar U S EPA Region 5 RPM

REQUIRED QAPP ELEMENT(S) AND CORRESPONDING QAPP SECTION(S) (U.S EPA, 2005a)	REQUIRED INFORMATION	CROSSWALK TO RELATED INFORMATION AND DOCUMENTS
Project Management and Objectives		
2 1 Title and Approval Page	▪ Title and Approval Page	Worksheet #1 Title and Approval Page
2 2 Document Format and Table of Contents	▪ Table of Contents ▪ QAPP Identifying Information	The Table of Contents is provided following the QAPP cover page Worksheet #2 Identifying Information
2 2 1 Document Control Format		
2 2 2 Document Control Numbering System		
2 2 3 Table of Contents		
2.2 4 QAPP Identifying Information		
2 3 Distribution List and Project Personnel Sign-Off Sheet	▪ Distribution List ▪ Project Personnel Sign-Off Sheet	Worksheet #3 Distribution List, and Worksheets #4-2 and #4-3 Project Personnel Sign Off Sheet
2 3 1 Distribution List		
2 3 2 Project Personnel Sign-Off Sheet		
2 4 Project Organization	▪ Project Organizational Chart ▪ Communication Pathways ▪ Personnel Responsibilities and Qualifications Table ▪ Special Personnel Training Requirements Table	Worksheets #5-4 and 5 5 Project Organization Charts Worksheet #6-4 and 6-5 Communication Pathways Worksheet #7 Personnel Responsibilities and Qualifications and Worksheet #8 Special Personnel Training Requirements
2 4 1 Project Organization Chart		
2 4.2 Communication Pathways		
2 4.3 Personnel Responsibilities and Qualifications		
2 4 4 Special Training Requirements and Certification		

QAPP Worksheet #2
Identifying Information

Project Management and Objectives (*Continued*)		
2 5 Project Planning/Problem Definition 2 5 1 Project Planning (Scoping) 2 5 2 Problem Definition, Site History and Background	▪ Project Planning Session ▪ Documentation (including Data Needs tables) ▪ Project Scoping Session Participants Sheet ▪ Problem Definition, Site History and Background ▪ Site Maps (historical and current)	Worksheet #8 Special Personnel Training Requirements Worksheets #9-6 and 9 7 Project Scoping Session Participants Sheet, and Worksheets #10-5 and 10-6 Problem Definition DQOs Site history and more detail concerning the project DQOs can be found in the companion documents to this Multi Area QAPP Site maps can be found on Figures 1 1 1 2 and 2 1 through 2 3
2 6 Project Quality Objectives and measurement Performance Criteria 2 6 1 Development of Project Quality Objectives Using the Systematic Planning Process 2 6 2 Measurement performance Criteria	▪ Site-Specific Project Quality Objectives (PQOs) ▪ Measurement Performance Criteria Table	Worksheets # 11 5 and 11 6 Project Quality Objectives/Systematic Planning Process Statements Worksheets #12 1 through 12 17 Measurement Performance Criteria
2 7 Secondary Data Evaluation	▪ Sources of Secondary Data and Information ▪ Secondary Data Criteria and Limitations Table	Worksheets #13 1 and 13 2 Secondary Data Criteria and Limitations
2 8 Project Overview and Schedule 2 8 1 Project Overview 2 8 2 Project Schedule	▪ Summary of Project Tasks ▪ Reference Limits and Evaluation Table ▪ Project Schedule/Timeline Table	Worksheet #14 Summary of Project Tasks Worksheets #15 1 through 15-4 Reference Limits and Evaluation and Worksheet #16 5 and 16-6 Project Schedules/Timelines

QAPP Worksheet #2
Identifying Information

Measurement/Data Acquisition		
3 1 Sampling Tasks 3 1 1 Sampling Process Design and Rationale 3 1 2 Sampling Procedures and Requirements 3 1 2 1 Sampling Collection Procedures 3 1 2 2 Sample Containers Volume and Preservation 3 1.2 3 Equipment/Sample Container Cleaning and Decontamination Procedures 3 1.2 4 Field Equipment Calibration, Maintenance Testing and Inspection Procedures 3 1 2 5 Supply Inspection and Acceptance Procedures 3 1.2 6 Field Documentation Procedures	▪ Sampling Design and Rationale ▪ Sample Location Map ▪ Sampling Locations and Methods/ SOP Requirements Table ▪ Analytical Methods/SOP Requirements Table ▪ Field Quality Control Sample Summary Table ▪ Sampling SOPs ▪ Project Sampling SOP References Table ▪ Field Equipment Calibration, Maintenance Testing and Inspection Table	Worksheet #17 5 and 17 6 Sampling Design and Rationale Worksheet #18-4 and 18 5 Sampling Locations and Methods/SOP Requirements Worksheet #19 Analytical SOP Requirements (sample containers preservation, and holding times) Worksheet #20 Field Quality Control Sample Summary Worksheet #21 Project Sampling SOP Reference and Worksheet #22 Field Equipment Calibration, Maintenance Testing and Inspection The laboratory SOPs can be found in Attachment 1 5 More details concerning the sampling design and rationale and the field sampling procedures can be found in the companion documents to this Multi Area QAPP
3 2 Analytical Tasks 3.2 1 Analytical SOPs 3 2 2 Analytical Instrument Calibration Procedures 3 2 3 Analytical Instrument and Equipment Maintenance Testing, and Inspection Procedures 3.2 4 Analytical Supply Inspection and Acceptance Procedures	▪ Analytical SOPs ▪ Analytical SOP References Table ▪ Analytical Instrument Calibration Table Analytical Instrument and Equipment Maintenance Testing and Inspection Table	Worksheet #23 Analytical SOP References Worksheet #24 Analytical Instrument Calibration and Worksheet #25 Analytical Instrument and Equipment Maintenance Testing, and Inspection The laboratory SOPs can be found in Attachment 1 5
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3 3 1 Sample Collection Documentation 3 3 2 Sample Handling and Tracking System 3 3 3 Sample Custody	▪ Sample Collection Documentation Handling, Tracking and Custody SOPs ▪ Sample Container Identification ▪ Sample Handling Flow Diagram Example Chain of Custody Record and Seal	Worksheet #27 Sample Custody Requirements More details concerning the field sampling procedures can be found in the companion documents to this Multi Area QAPP Example COC forms can be found in Attachment 1 3

QAPP Worksheet #2
Identifying Information

Measurement/Data Acquisition (*continued*)		
3 4 Quality Control Samples 3 4 1 Sampling Quality Control Samples 3 4 2 Analytical Quality Control Samples	▪ QC Samples Table ▪ Screening/Confirmatory Analysis Decision Tree	Worksheet #28 1 through #28 21 Present QC sample information for project analysis
3 5 Data Management Tasks 3 5 1 Project Documentation and Records 3 5 2 Data Package Deliverables 3 5 3 Data Reporting Formats 3 5 4 Data Handling and Management 3 5 5 Data Tracking and Control	▪ Project Documents and Records Table ▪ Analytical Services Table ▪ Data Management SOPs	Worksheet #29 Project Documents and Records, and Worksheet #30 Analytical Services
4 1 Assessments and Response Actions 4 1 1 Planned Assessments 4 1 2 Assessment Findings and Corrective Action Responses	▪ Assessments and Response Actions ▪ Planned Project Assessments Table ▪ Audit Checklists ▪ Assessment Findings and Corrective Action Responses Table	Worksheet #31 Planned Project Assessments and Worksheet #32 Assessment Findings and Corrective Action Responses The laboratory Quality Assurance Manual and Laboratory Policies and Guidelines documents can be found in Attachments 1-4 and 1 6 respectively
4 2 QA Management Reports	▪ QA Management Reports Table	Worksheet #33 QA Management Reports
4 3 Final Project Report		

QAPP Worksheet #2
Identifying Information

Data Review		
5 1 Overview		
5 2 Data Review Steps	▪ Verification (Step I) Process Table ▪ Validation (Steps IIa and IIb) Process Table ▪ Validation (Steps IIa and IIb) Summary Table ▪ Usability Assessment	Worksheet #34 Verification (Step 1) Process Worksheet #35 Validation (Step I) Process Worksheet #36 Validation (Steps IIa and IIb) Summary and Worksheet #37 Usability Assessment.
5 2 1 Step I Verification		
5 2 2 Step II Validation		
5.2 2 1 Step IIa Validation Activities		
5 2 2 2 Step IIb Validation Activities		
5 2 3 Step III Usability Assessment		
5 2 3 1 Data Limitations and Actions from Usability Assessment		
5.2.3 2 Activities		
5 3 Streamlining Data Review	▪ None	NA
5 3 1 Data Review Steps To Be Streamlined		
5 3 2 Criteria for Streamlining Data Review		
5.3 3 Amounts and Types of Data Appropriate for Streamlining		

QAPP Worksheet #3
Distribution List

QAPP RECIPIENTS	TITLE	ORGANIZATION	TELEPHONE NUMBER	E-MAIL ADDRESS	DOCUMENT CONTROL NUMBER
Michael Berkoff (2 copies)	Remedial Project Manager 12th Street Landfill	U S EPA Region 5	312 353 8983	berkoff michael@epa gov	56394 (3)-001
Sam Chummar (2 copies)	Remedial Project Manager Plainwell Mill	U S EPA Region 5	312.886 1434	chummar sam@epamail epa gov	56394 (3)-001
Richard Gay	Environmental Manager	Weyerhaeuser	501 624 8554	richard gay@weyerhaeuser com	56394 (3)-001
Martin Lebo	Senior Aquatic Scientist	Weyerhaeuser	252 633 7511	martin.lebo@weyerhaeuser com	56394 (3)-001
Gregory Carli	Project Manager	CRA	905 682.0510	gcarli@craworld com	56394 (3)-001
Emily Stahl	Project Coordinator (Plainwell Mill)	CRA	905 682 0510	estahl@craworld com	56394 (3)-001
Jodie Dembowske	Project Coordinator (12th Street Landfill)	CRA	269.344 1230	jdembowske@craworld com	56394 (3)-001
Paul Wiseman	QA Officer	CRA	734 453 5123	pwiseman@craworld com	56394 (3)-001
Golnoush Bolourani	Field QA Officer	CRA	905 682 0510	gbolourani@craworld com	56394 (3)-001
Dennis Catalano	Laboratory Manager	WATS	253 924 6242	dennis catalano@weyerhaeuser com	56394 (3) 001
Jeff Christian	Laboratory Manager	CAS	360 577 7222	jchristian@caslab com	56394 (3) 001

QAPP Worksheet #4-2
Project Personnel Sign-Off Sheet (WATS)

PROJECT PERSONNEL	TITLE	TELEPHONE NUMBER	SIGNATURE	DATE QAPP READ
Dennis Catalano	Laboratory Manager	253 924 6242		

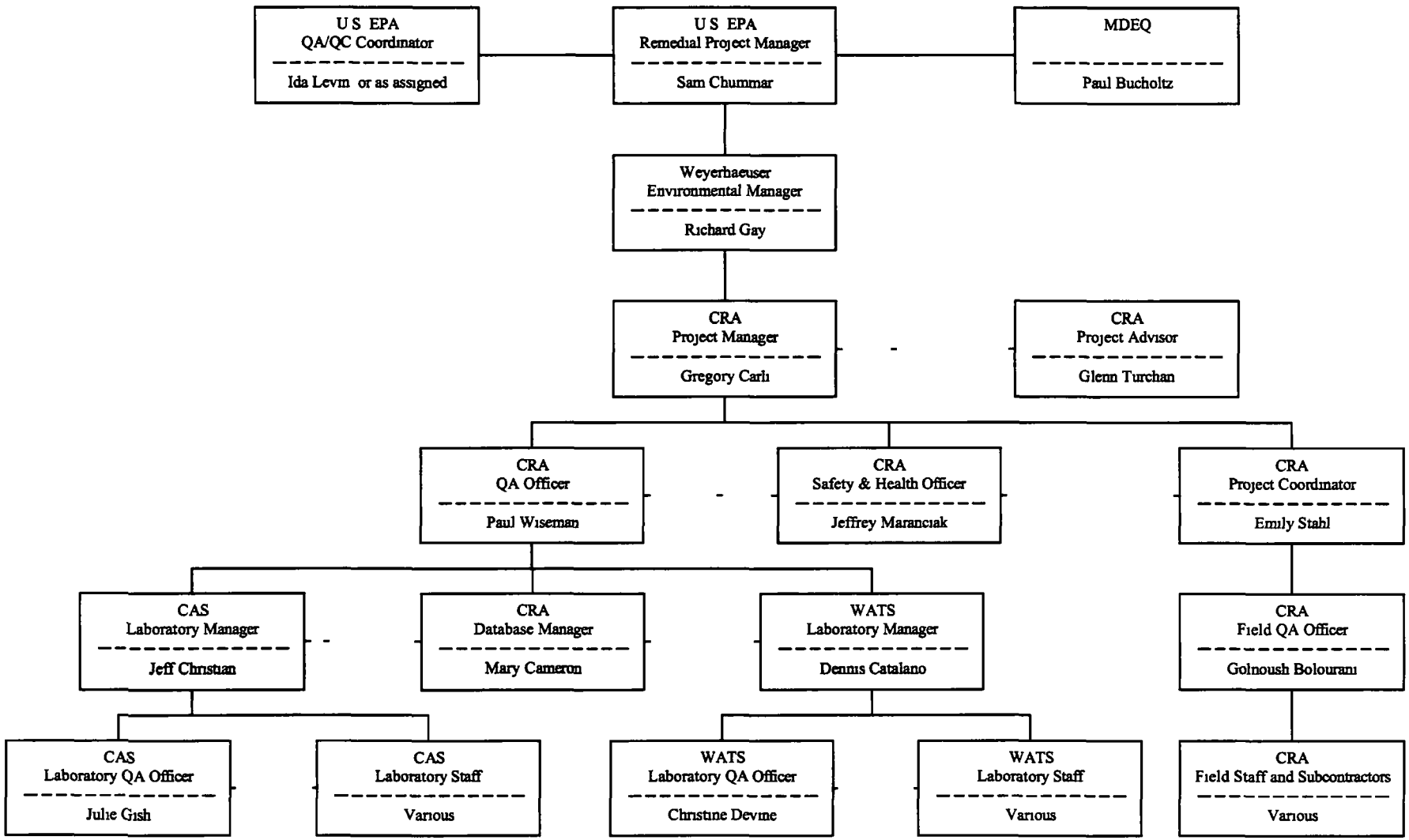
QAPP Worksheet #4-3
Project Personnel Sign-Off Sheet (CAS)

PROJECT PERSONNEL	TITLE	TELEPHONE NUMBER	SIGNATURE	DATE QAPP READ
Jeff Christian	Laboratory Manager	360 557 7222		

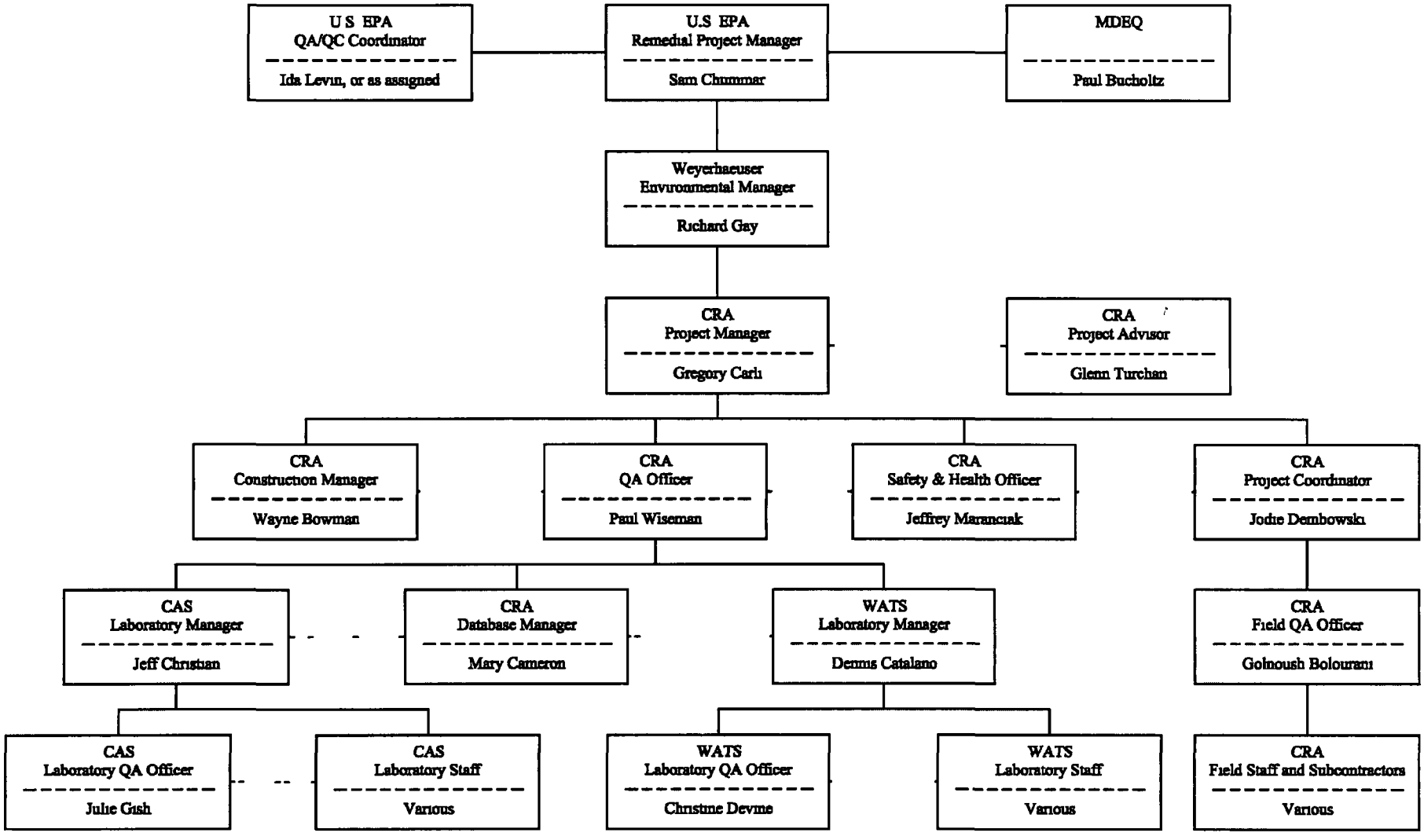
QAPP Worksheet #4-4
Project Personnel Sign-Off Sheet (CRA)

PROJECT PERSONNEL	TITLE	TELEPHONE NUMBER	SIGNATURE	DATE QAPP READ
Gregory Carli	Project Manager	905 682 0510		
Paul Wiseman	QA Officer	734 453 5123		
Golnoush Bolourani	Field QA Officer	905 682 0510		

QAPP Worksheet # 5-4
Project Organizational Chart
Plainwell Mill Phase II RI Work Plan



QAPP Worksheet # 5-5
Project Organizational Chart
12th Street Landfill Remedial Action Work Plan



QAPP Worksheet #6-4
Communication Pathways
Plainwell Mill Phase II RI Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Phase II RI Work Plan- Former Plainwell, Inc Mill Property				
Serve as Point-of-Contact with U S EPA Remedial Project Manager (RPM)	Environmental Manager	Richard Gay Weyerhaeuser	501 624 8554	Richard Gay will provide project submittals to Sam Chummar U S EPA, in accordance with the schedule provided on Worksheet No 16 of this QAPP
Manage all project phases	Project Manager	Gregory Carli CRA	905 682 0510	Gregory Carli will be the CRA liaison to the U S EPA for activities at the Plainwell Mill and 12th Street Landfill properties
Coordination of project activities under supervision of Gregory Carli	Project Coordinator	Emily Stahl CRA	905 682 0510	Emily Stahl will provide Gregory Carli with an update of project activities including data review and display data evaluation and analysis sampling plan preparation and supervision of implementation field sampling activities Emily Stahl will report any QA/QC problems related to field measurements to the QA Officer (Paul Wiseman) by telephone or e mail by the end of the same business day
Provide assistance with Site Specific Health and Safety	Safety & Health Officer	Jeffery Maranciak, CRA	412 449 0812	Jeffery Maranciak will provide assistance to Project Coordinator and Field QA Officer (Golnoush Bolourani) with Site Specific Health and Safety Orientation to all CRA staff Jeffery Maranciak will provide Gregory Carli with any problems related to filed health and safety concerns

QAPP Worksheet #6-4
Communication Pathways
Plainwell Mill Phase II RI Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc)
Notify Gregory Carli Emily Stahl, and the QA Officer of any QAPP changes in the field	Field QA Officer	Golnoush Bolourani CRA	905 682 0510	Golnoush Bolourani will provide Gregory Carli and Emily Stahl with daily progress report on implementation of field activities and any changes to the QAPP made in the field by e mail or fax within 2 business days Golnoush Bolourani will also provide Gregory Carli and Emily Stahl with any QA/QC problems related to field measurements by telephone or e mail by the end of the same business day
Reporting lab data quality issues	Laboratory Manager	Dennis Catalano WATS	253 924 6242	Dennis Catalano will notify the QA officer (Paul Wiseman) with any QA/QC issues within 2 business days
Reporting lab data quality issues	Laboratory Manager	Jeff Christian, CAS	360 557 7222	Jeff Christian will notify the QA officer (Paul Wiseman) with any QA/QC issues within 2 business days
Field and analytical corrective actions	QA Officer	Paul Wiseman, CRA	734 453 5123	Paul Wiseman will determine the need for corrective action for field and analytical issues in conjunction with the Gregory Carli and Emily Stahl or the Laboratory Manager as appropriate
Release of final analytical data	QA Officer	Paul Wiseman, CRA	734 453 5123	No final analytical data can be released until validation is complete and Paul Wiseman has approved the release
QAPP amendments	QA Officer	Paul Wiseman CRA	734 453 5123	Any major changes to the QAPP must be approved by Paul Wiseman, Gregory Carli and the U S EPA before the changes can be implemented
Establish and maintenance of project database	Database Manager	Mary Cameron	734 453 5123	Mary Cameron will provide analytical data to Paul Wiseman and Rawa Fleisher

QAPP Worksheet #6-5
Communication Pathways
12th Street Landfill Remedial Action Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Remedial Action (RA) – 12th Street Landfill				
Serve as Point of-Contact with U S EPA Remedial Project Manager (RPM)	Environmental Manager	Richard Gay Weyerhaeuser Company	501 624 8554	Richard Gay will provide project submittals to Michael Berkoff U S EPA in accordance with the schedule provided on Worksheet No 16 of the QAPP
Manage all project phases	Project Manager	Gregory Carli CRA	905 682 0510	Gregory Carli will be the CRA liaison to the U S EPA for activities at the Plainwell Mill and 12th Street Landfill properties
Coordination of project activities under supervision of Gregory Carli	Project Coordinator	Jodie Dembowske CRA	412 449 0812	Jodie Dembowske will provide Gregory Carli with an update of project activities including data review and display data evaluation and analysis sampling plan preparation and supervision of implementation field sampling activities Jodie Dembowske will report any QA/QC problems related to field measurements to the QA Officer (Paul Wiseman) by telephone or e-mail by the end of the same business day
Provide assistance with construction and redevelopment	Construction Manager	Wayne Bauman, CRA	269 344 1230	Wayne Bauman will provide Gregory Carli with an update of construction activities including related questions or problems by telephone or e mail at the end of each business day
Provide assistance with Site Specific Health and Safety	Safety & Health Officer	Jeffery Maranciak, CRA	412 449 0812	Jeffery Maranciak will provide assistance to Project Coordinator and Field QA Officer (Golnoush Bolourani) with Site Specific Health and Safety Orientation to all CRA staff Jeffery Maranciak will provide Gregory Carli with any problems related to filed health and safety concerns

QAPP Worksheet #6-5
Communication Pathways
12th Street Landfill Remedial Action Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Notify Gregory Carli Jodie Dembowske and the QA Officer of any QAPP changes in the field	Field QA Officer	Golnoush Bolourani CRA	905 682 0510	Golnoush Bolourani will provide Gregory Carli and Jodie Dembowske with daily progress report on implementation of field activities and any changes to the QAPP made in the field by e mail or fax within 2 business days Golnoush Bolourani will also provide Gregory Carli and Jodie Dembowske with any QA/QC problems related to field measurements by telephone or e mail by the end of the same business day
Reporting lab data quality issues	Laboratory Manager	Dennis Catalano WATS	253 924 6242	Dennis Catalano will notify the QA Officer (Paul Wiseman) with any QA/QC issues within 2 business days
Reporting lab data quality issues	Laboratory Manager	Jeff Christian, CAS	360 557 7222	Jeff Christian will notify the QA Officer (Paul Wiseman) with any QA/QC issues within 2 business days
Field and analytical corrective actions	QA Officer	Paul Wiseman, CRA	734 453 5123	Paul Wiseman will determine the need for corrective action for field and analytical issues in conjunction with the Gregory Carli and Jodie Dembowske or the Laboratory Manager as appropriate
Release of final analytical data	QA Officer	Paul Wiseman, CRA	734 453 5123	No final analytical data can be released until validation is complete and Paul Wiseman has approved the release
QAPP amendments	QA Officer	Paul Wiseman, CRA	734 453 5123	Any major changes to the QAPP must be approved by Paul Wiseman, Gregory Carli and the U S EPA before the changes can be implemented
Development and maintenance of database	Database Manager	Mary Cameron	734 453 5123	Mary Cameron will provide analytical data to Paul Wiseman and Rawa Fleisher

QAPP Worksheet #7
Personnel Responsibilities and Qualifications

NAME	PROJECT ROLE	ORGANIZATIONAL AFFILIATION	EDUCATION AND EXPERIENCE QUALIFICATIONS
Michael Berkoff Sam Chummar	Remedial Project Manager 12th Street Landfill Remedial Project Manager Plainwell Mill	U S EPA Region 5	Designated as the U S EPA s Project Coordinators
Richard Gay	Environmental Manager	Weyerhaeuser	Designated as the Weyerhaeuser Project Manager
Gregory Carli P E	Project Manager	CRA	B.A.Sc Civil Engineering, Water Resources Option, University of Waterloo 1996 Over 13 years of experience
Glenn Turchan, P E	Project Director	CRA	B A Sc Geological Engineering, University of Waterloo M A.Sc Civil Engineering, University of Waterloo Over 24 years of experience
Emily Stahl	Project Coordinator Plainwell Mill	CRA	B Sc Earth Surface Science University of Guelph Over 5 years experience
Jodie Dembowske	Project Coordinator 12th Street Landfill	CRA	M Sc Hydrogeology Western Michigan University 1994 B Sc Geology Western Michigan University 1991 Over 16 years experience
Paul Wiseman	QA Officer	CRA	B Sc Chemistry and Biology Northern Michigan University 1980 Over 29 years experience
Wayne Bauman	Construction Manager – 12th Street Landfill	CRA	B A.Sc Industrial Engineering, Minor Mathematics Western Michigan University 1986 Over 23 years experience
Jeffrey Maranciak	Safety & Health Officer	CRA	B S Safety & Environmental Management Slippery Rock University 1997 Over 12 years experience
Dennis Catalano	Laboratory Manager	WATS	B.S Biology with chemistry minor University of Dayton, 1977 30 years of experience

QAPP Worksheet #7
Personnel Responsibilities and Qualifications

NAME	PROJECT ROLE	ORGANIZATIONAL AFFILIATION	EDUCATION AND EXPERIENCE QUALIFICATIONS
Christine Devine	Laboratory QA/QC Officer	WATS	B .Sc Mathematics University of Washington 1998 M.A.Sc Analytical Chemistry Illinois Institute of Technology 2007 Over 10 years of experience
Jeff Christian	Laboratory Manager	CAS	B.S Chemistry Evergreen State College 1993 Over 30 years of experience
Julie Gish	Laboratory QA/QC Officer	CAS	B .Sc Food Science Utah State University 1975 M A Sc Food Science Oregon State University 1978 Over 30 years of experience
Golnoush Bolourani	Field QA Officer	CRA	B A Sc Materials Science and Engineering, University of Toronto 2004 M A Sc Environmental Engineering, Concordia University 2008 Over 3 years of experience
Mary Cameron	Database Manager	CRA	B Sc Microbiology University of Michigan, 1984 Assoc Computer Information Systems Henry Ford Community College Dearborn, Michigan 2001 Over 18 years of experience

U S EPA

Remedial Project Manager

- Serve as the primary point of contact for the U S EPA
- Review and approve project submittals
- Coordinate with the Michigan DEQ and other regulatory agencies as needed
- Monitor project activities

QA/QC Coordinator

- Review and approve the QAPP
- Review and approve relevant portions of submitted documents to ensure compliance with the QAPP
- Coordinate audits as necessary

WEYERHAEUSER COMPANY

Environmental Manager

- Serve as the primary point-of contact between Weyerhaeuser Company and the U S EPA
- Coordinate communications between Weyerhaeuser CRA, the U S EPA and other parties
- Review draft project deliverables prior to their submittal to the U S EPA

CRA

Project Manager

- Serve as the primary point of-contact for CRA
- Communicate with Weyerhaeuser Company the U S EPA, and other project stakeholders
- Establish and communicate project milestones and schedules
- Coordinate and review CRA work products
- Direct CRA team members

  Provide technical input during the planning design, and implementation stages of the project

  Review the technical aspects of CRA s submittals

  Approval of Quality Assurance Project Plan (QAPP)
- Preparation & Review of QAPP

Project Director

- Provide overall quality assurance including a review of CRA s performance on the project.
- Review project progress and CRA work products for compliance with project objectives and requirements
- Provide input regarding Superfund procedures and compliance with the National Contingency Plan (NCP)

Project Coordinator

- Review existing data, project objectives and regulatory guidance to assist in the development of project sampling protocols
- Review and summarize the results of data collected during project implementation, and make preliminary recommendations to the CRA Project Manager regarding the results (*e g* whether additional data collection or field modifications appear to be necessary)

Field QA Officer

- Coordinate environmental staff who will be measuring and recording field parameters collecting samples and documenting construction activities to ensure compliance with this QAPP
- Order sample bottles from the laboratory

  Prepare reports pertaining to relevant field activities
- Maintain field and laboratory files including project documentation, sample logs and calculations and provide complete copies to the CRA Project Coordinator
- Conduct field audits as necessary

Safety Health Officer

- Provide assistance to the Field QA Officer and on Site staff with Site specific Health and Safety Orientation to all CRA staff and subcontractors and monitoring site activities for compliance with the project Health and Safety Plan

Construction Manager

Coordinate and direct subcontractors and CRA personnel who are performing construction work (*e g* site preparation, excavation)

- Assist Field QA Officer with Health and Safety Orientations for construction related activities
- Maintain field records related to construction activities and provide complete copies to the CRA Project Manager

QA Officer

- Serve as the primary point of-contact with the laboratory
- Coordinate field QA/QC procedures with the Project Coordinator (*e g* calibrations for field analytical measurements and field audits as necessary) and review pertinent field records for compliance with this QAPP
- Review laboratory QA/QC procedures and documentation, as provided in data deliverables

  Review data for compliance with the Data Quality Objectives (DQOs) for the project

  Coordinate data validation activities and QA/QC reports preparation

Database Manager

- Establish and maintain a project database

  Import electronic data deliverables (EDDs) provided by the laboratory into the project database
- Perform a QA/QC check of imported data versus the hard copy data.
- Transcribe field and non EDD laboratory data into the project database as necessary

Tabulate data for end users

ANALYTICAL LABORATORY

Laboratory Manager

Serve as the primary point of-contact for the laboratory

Oversee preparation of analytical reports

- Supervise in house chain of custody

Laboratory QA/QC Officer

- Maintains laboratory quality assurance procedures
- Maintains laboratory QA/QC documentation
- Verify that the laboratory meets the QA/QC standards specified in this QAPP
- Perform laboratory audits in accordance with this QAPP

QAPP Worksheet #8
Special Personnel Training Requirements

PROJECT FUNCTION	SPECIALIZED TRAINING - TITLE OR DESCRIPTION OF COURSE	TRAINING PROVIDER	TRAINING DATE	PERSONNEL/ GROUPS RECEIVING TRAINING	PERSONNEL TITLES/ ORGANIZATIONAL AFFILIATION	LOCATION OF TRAINING RECORDS/ CERTIFICATES
Field activities	40-hour HAZWOPER and 8 hour HAZWOPER refresher	Certified training professionals	8 hour refresher within previous year	Field personnel	CRA personnel	CRA project offices
Confined Space Entry	Confined space training and testing if applicable	Certified training professionals	4 hour training	Field personnel	CRA personnel	CRA project offices
Analytical chemistry	No state laboratory certification program in Michigan(1)	N/A	N/A	N/A	Weyerhaeuser Analysis and Testing Services (WATS) Weyerhaeuser Company Mail Stop WTC2F25 32901 Weyerhaeuser Way Federal Way WA 98001 Dennis Catalano 253 924 6242	N/A

QAPP Worksheet #8
Special Personnel Training Requirements

PROJECT FUNCTION	SPECIALIZED TRAINING TITLE OR DESCRIPTION OF COURSE	TRAINING PROVIDER	TRAINING DATE	PERSONNEL/ GROUPS RECEIVING TRAINING	PERSONNEL TITLES/ ORGANIZATIONAL AFFILIATION	LOCATION OF TRAINING RECORDS/ CERTIFICATES
Analytical chemistry	No state laboratory certification program in Michigan[1]	N/A	N/A	N/A	Columbia Analytical Services (CAS) 1317 S 13th Avenue Kelso WA 98626 Jeff Christian 360 577 7222	N/A

Footnote

(1) WATS and CAS are certified by the State of Washington.

QAPP Worksheet #9 6
Project Scoping Session Participants Sheet (May/June 2009)

Project Name Former Plainwell Inc Mill Property

Projected Date(s) of Sampling 2009 **Site Name** Allied Paper, Inc /Portage Creek/Kalamazoo River Superfund Site

CRA Project Managers Gregory Carli **Location of Scoping Session** Conference Call

Date of Sessions May 20 2009 Phase II RI Work Plan and June 17 2009 Conference Call

Scoping Session Purpose To discuss the Phase II RI Work Plan

NAME	TITLE	AFFILIATION	TELEPHONE NUMBER	E-MAIL ADDRESS	PROJECT ROLE
Sam Chummar	Remedial Project Manager	U S. EPA Region 5	312 353 8983	chummar sam@epa gov	U S EPA Project Manager
Richard Gay	Environmental Manager	Weyerhaeuser	501 624 8554	richard gay@weyerhaeuser com	Weyerhaeuser Environmental Manager
Martin Lebo	Senior Aquatic Scientist	Weyerhaeuser	252 633 7511	martin.lebo@weyerhaeuser com	Technical Assistance
Gregory Carli	Project Manager	CRA	905 682 0510	gcarli@craworld com	CRA Project Manager
Emily Stahl	Project Coordinator	CRA	905 682 0510	estahl@craworld com	CRA Project Coordinator

QAPP Worksheet #9-6
Project Scoping Session Participants Sheet (May/June, 2009)

Comments/Decisions

- Discussion and comment regarding the proposed analyte list.
- As applicable Weyerhaeuser will identify potential scenarios under which field modifications (e g additional test pits, changes in location or methods) may be needed

Action Items

- Respond to Comments and submit the revised Work Plan – completed (05/20/2009)

Consensus Decisions

- Characterization of material for offsite disposal will include a PID measurements

  Characterization of material selected for disposal will be disposed of properly according to applicable state and federal regulations
- Need to submit a full work plan for the Plainwell Mill RI/FS

QAPP Worksheet #9-7
Project Scoping Session Participants Sheet (April-June, 2009)

Project Name 12th Street Landfill

Projected Date(s) of Sampling: 2009/2010 **Site Name** Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site

CRA Project Managers Gregory Carli **Location of Scoping Session.** Conference Call

Date of Sessions Conference Calls on April 17 2009 and May 1 2009

Scoping Session Purpose: To discuss the revisions to the Remedial Design

NAME	TITLE	AFFILIATION	TELEPHONE NUMBER	E-MAIL ADDRESS	PROJECT ROLE
Michael Berkoff	Remedial Project Manager	U S EPA Region 5	312 353 8983	chummar sam@epa gov	U S EPA Project Manager
Paul Bucholtz	Superfund Section Specialized Sampling Unit Project Manager	MDEQ	517 373 8174	bucholtp@michigan gov	MDEQ Project Manager
Richard Gay	Environmental Manager	Weyerhaeuser	501 624 8554	richard gay@weyerhaeuser com	Weyerhaeuser Environmental Manager
Martin Lebo	Senior Aquatic Scientist	Weyerhaeuser	252 633 7511	martin.lebo@weyerhaeuser com	Technical Assistance
Gregory Carli	Project Manager	CRA	905 682 0510	gcarli@craworld com	CRA Project Manager
Jodie Dembowske	Project Coordinator	CRA	269 344 1230	jdembowske@craworld com	CRA Project Coordinator

QAPP Worksheet #9-7
Project Scoping Session Participants Sheet (April-June, 2009)

Comments/Decisions.

- Concept of design changes mainly landfill slope from 4 1 to 3 1
- Does not impact post excavation sampling approach.

Action Items

- Prepare Pre-Final Design Report Addendum No 1 in three Submittals

Consensus Decisions

- Concept of design changes agreeable to all partners pending review of design submittals

QAPP Worksheet #10 5
Problem Definition DQOs
Plainwell Mill Phase II RI Work Plan

Step 1 State the problem

As approved by U S EPA on August 6 2008 the Remedial Investigation is being implemented in a phased approach The Phase II RI Work Plan is in accordance with Statement of Work (SOW) for the Remedial Investigation and Feasibility Study and the terms of the Consent Decree for the Design and Implementation of Certain Response Actions at Operable Unit #4 and the Plainwell, Inc Mill Property of the Allied Paper Inc./Portage Creek/Kalamazoo River Superfund Site (Consent Decree) which became effective February 22 2005

From early 1950s to 1970s carbonless papers were recycled at the mill a process that released a waste stream containing PCBs to Kalamazoo River In addition until the early 1950s wastewater from paper making operations were discharged directly to the Kalamazoo River By the mid 1950s wastewater treatment facilities were in place at the Site and in late 1960s the treatment facilities improved In early 1980s the treatment facilities were improved by construction of a new wastewater treatment facility consisting of a new primary clarifier a mechanical dewatering system a new secondary clarifier and an activated sludge treatment system

This Phase II RI Work Plan includes field sampling and analysis activities, consisting of a soil and supplemental groundwater investigation which are required to complete the RI pursuant to the SOW and constitutes the final phase of the RI

Step 2 Identify the goal of the study

The key goals of the data collection activities for the Phase II RI Work Plan as follows

Perform a supplemental groundwater investigation to further evaluate the nature and extent of impacts to groundwater and their potential sources

- Further assess shallow site-specific hydrogeologic characteristics and interconnections with the Kalamazoo River and
- Perform soil investigations in the former wastewater sludge and dewatering lagoon and aeration basin area, the area of the mill buildings and the north central portion of the mill, to adequately characterize the nature and extent of impacts to soil in the unsaturated zone that may have occurred due to historical operations of the mill.

Step 3 Identify information inputs

Decision inputs for Phase II RI Work Plan are to determine the nature and extent of the contamination to assess risk and support development and evaluation of remedial alternatives to evaluate potential risk, and to develop and evaluate remedial alternatives

Step 4 Define the boundaries of the sampling

The area considered as part of this action includes the Plainwell, Inc Mill Property located at 200 Allegan Street, Plainwell, Michigan (see Figure 2-4)

QAPP Worksheet #10-5
Problem Definition DQOs
Plainwell Mill Phase II RI Work Plan

Step 5 Develop the analytical approach.
Surface water samples will be analyzed for low level mercury methyl mercury and hardness Soil samples will be analyzed for Target Compound List (TCL) VOCs TCL SVOCs PCBs Target Analyte List (TAL) metals Synthetic Precipitation Leaching Procedure (SPLP) metals, and general chemistry and Groundwater from monitoring locations will be analyzed for TCL VOCs TAL SVOCs PCBs and TAL inorganics In addition two surface water samples will be collected and analyzed for low level mercury methyl mercury and hardness
Step 6 Specify performance or acceptance criteria.
The acceptance criteria for the Phase II RI Work Plan activities are having collected sufficient information to meet the study objectives described under Step 2 above and sufficient information to proceed with the investigation If these criteria are not met, additional data will be collected in a similar manner to meet these objectives
Step 7 Develop the plan for obtaining the data.
The overall QA objective is to develop and implement procedures for field sampling that will provide results to support the evaluation of site data consistent with Michigan Part 201 Generic Residential Cleanup Criteria (GRCC) requirements In general soil and groundwater sampling will be performed to provide representative adequate number of samples Specific procedures for sampling chain of custody instrument calibration, analysis reporting and internal quality control are described in other worksheets of this QAPP

QAPP Worksheet #10-6
Problem Definition DQOs
12th Street Landfill Remedial Action Work Plan

Step 1 State the problem.

Operable Unit #4 (OU-4) of the Allied Paper Inc./Portage Creek/Kalamazoo River Superfund Site (Kalamazoo River Superfund Site) consists of the former 12th Street Landfill and the four areas outside the landfill where PCB-contaminated residual material has been observed. The 6 5 acre landfill is situated on an approximately 24-acre property with about 17 acres of wetlands The additional portions of OU-4 that are located outside the landfill property include the woodland area owned by the State of Michigan (State) under the management of the Michigan Department of Natural Resources (MDNR) the asphalt plant operation adjacent to the landfill, and the former powerhouse discharge channel A Record of Decision (ROD) for OU-4 was issued on September 28 2001

The scope of the RA for the 12th Street Landfill includes excavation of paper residuals present outside the footprint of the landfill (on adjacent properties) landfill grading the construction of a landfill cover and erosion protection measures and surface water management, landfill gas management, construction of access road, abandonment of existing groundwater monitoring wells installation of groundwater monitoring wells and various environmental monitoring activities

Step 2 Identify the goal of the study

The key goals of the activities for the RA Work Plan investigations are as follows

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- Confirmation of removal of paper residuals from the wetland north of landfill in accordance with the RA activities required by the ROD

Asphalt Plant Property

Confirmation of removal of paper residuals from the asphalt plant property in accordance with the RA activities required by the ROD

MDNR Properties

Confirmation of removal of paper residuals from the MDNR property in accordance with the RA activities required by the ROD

Landfill Grading

To implement an effective grading plan to prevent or minimize potential off site damages and

To construct a final cover over the regarded landfill sideslopes and top portion of the landfill to meet the ROD requirements

Landfill Gas Management

- To collect readily accessible information about the subsurface landfill gas conditions at the 12th Street Landfill that may be useful in designing a passive gas venting system for the landfill

QAPP Worksheet #10-6
Problem Definition DQOs
12th Street Landfill Remedial Action Work Plan

Step 3 Identify information inputs
Removal of Paper Residuals Beyond Landfill Footprint ***Wetland*** Information inputs will include visual observations of extent of paper residuals base on color and consistency in accordance the ROD ***Asphalt Plant Property*** Information inputs will include visual observations of extent of paper residuals base on color and consistency in accordance the ROD and Collection of verification sampling ***MDNR Properties*** Information inputs will include visual observations of extent of paper residuals base on color and consistency in accordance the ROD and Collection of verification sampling ***Grading Design*** ▪ Information inputs will include global slope stability modeling to access the potential effect of the moisture and shear strength to meet requirements of State of Michigan solid waste management regulations (Part 115) ***Landfill Gas Management*** The information that is collected for determining the extent of paper residuals beyond the landfill footprint and for the grading design will be supplemented with similar visual information recorded during previous investigations at the 12th Street Landfill site
Step 4 Define the boundaries of the sampling
The area considered as part of this action includes the 12th Street Landfill located at Plainwell, Michigan (see Figure 2 5)
Step 5 Develop the analytical approach.
Soil samples collected from Asphalt Property will be analyzed for TCL VOCs and PCBs and Soil samples collected from MDNR Properties will be analyzed for PCBs
Step 6 Specify performance or acceptance criteria.
The acceptance criteria for the Remedial Action Work Plan activities are having collected sufficient information to meet the study objectives described under Step 2 above and sufficient information to proceed with the investigation. If these criteria are not met, additional data will be collected in a similar manner to meet these objectives
Step 7 Develop the plan for obtaining the data.
The overall QA objective is to develop and implement procedures for field sampling that will provide results to support the evaluation of site data consistent with Michigan Part 201 Generic Residential Cleanup Criteria (GRCC) requirements In general soil sampling will be performed to provide representative adequate number of samples Specific procedures for sampling, chain of-custody instrument calibration, analysis, reporting and internal quality control are described in other worksheets of this QAPP

QAPP Worksheet #11 5
Project Quality Objectives/Systematic Planning Process Statements
Plainwell Mill Phase II RI Work Plan

Who will use the data?

Weyerhaeuser CRA, and the overseeing agencies including the U S EPA and the MDEQ will use the data.

What will the data be used for?

Surface Water Sampling

The surface water data will be used to assess the compliance with applicable MDEQ Part 201 Criteria to determine the next steps

Soil Sampling Activities

The soil data will be used to assess the compliance with applicable MDEQ Part 201 Criteria to further characterize the soil quality at the mill

Groundwater Monitoring

The groundwater data will be used to assess the compliance with applicable MDEQ Part 201 Criteria to determine the next steps of investigations and characterize the groundwater flow direction.

What types of data are needed (target analytes, analytical groups, field screening, on-site analytical or off site laboratory techniques, sampling techniques)?

Sampling and analytical protocols are defined later in this document.

Surface Water Sampling:

Surface water samples will be analyzed for low level mercury methyl mercury and hardness

Soil Sampling Activities

Soil samples collected will be analyzed for TCL VOCs TCL SVOCs PCBs TAL metals SPLP metals and general chemistry

Groundwater Monitoring:

Groundwater samples collected will be analyzed for TCL VOCs TAL SVOCs PCBs and TAL inorganics

QAPP Worksheet #11-5
Project Quality Objectives/Systematic Planning Process Statements
Plainwell Mill Phase II RI Work Plan

How "good" do the data need to be in order to support the environmental decision?

Field parameter data must be collected with a meter that has a precision of at least ±0 01 pH unit, ±0 001 milliSiemen per centimeter (mS/cm) for conductivity ±0 1 degree Celsius (C) for temperature ±0 1 millivolts (mV) for dissolved oxygen, ±0 1 nephelometric turbidity units (NTUs) for turbidity all data should be collected with a similar meter calibrated per the manufacturer's requirements

Surface Water Sampling:

To meet the objectives representative surface water will be collected based on the hydrology and morphometrics at two locations at the millrace and Kalamazoo River to confirm the surface water quality Samples collected for mercury (Hg) will be analyzed for low level mercury methyl mercury and hardness in accordance with the performance standards of EPA Method.

Soil Sampling Activities

Soil samples collected will be analyzed for TCL VOCs TCL SVOCs PCBs TAL metals, SPLP metals and general chemistry in accordance with the performance standards of EPA Methods

Groundwater Monitoring

Groundwater samples collected will be analyzed for TCL VOCs TAL SVOCs PCBs, and TAL inorganics in accordance with the performance standards of EPA Methods

How much data are needed (number of samples for each analytical group, matrix, and concentration)?

Surface Water Sampling

A minimum of two surface water samples will be collected to characterize the surface water quality at the millrace and Kalamazoo River

Soil Sampling Activities

Approximately 70 soil samples at various depths/locations will be collected to characterize the soil at the mill

Groundwater Monitoring

A minimum of 20 groundwater samples will be collected from existing and new monitoring well locations to further characterize the groundwater beneath the mill

QAPP Worksheet #11-5
Project Quality Objectives/Systematic Planning Process Statements
Plainwell Mill Phase II RI Work Plan

Where, when, and how should the data be collected/generated?

Surface Water Quality Monitoring:

- Field parameters will be taken prior sample collection. Samples will be collected at two locations southeastern of the mill from the millrace and northeastern portion of the mill from Kalamazoo River Samples will be collected according to the Phase II RI Work Plan schedule provided to the U S EPA The samples will be collected from either a boat or a shore-mounted semipermanent pier

Soil Sampling Activities

- Soil samples will be collected at various locations according to Phase II RI Work Plan at various locations/depths Soil samples will be collected according to the Phase II RI Work Plan schedule provided to U S EPA Specific sampling methods will depend upon the depth soil sample is collected from. At each location a foot soil core will be collected and examined in the field for visual and/or olfactory evidence of impact. Additionally soil cores will be screened across their entire length with a photoionization detector (PID) to determine the presence of undifferentiated volatile organic vapors Evidence of visual olfactory or PID impacts will be recorded along with a description of the soil, in accordance with the Universal Soil Classification System (USCS)

Groundwater Monitoring

- Site wide groundwater sampling will be conducted at the existing and new monitoring locations across the mill Groundwater samples will be collected according to the Phase II RI Work Plan schedule provided to U S EPA Monitoring wells will be purged using low flow sampling techniques to minimize drawdown and sediment agitation. Well purging will continue until three consecutive and consistent readings of the stabilization parameters (i e pH, temperature conductivity turbidity oxygen reduction potential, and dissolved oxygen) are obtained.

Who will collect and generate the data?

CRA field personnel will collect the samples the laboratories (WATS and CAS) will analyze the collected field samples and issue data reports and CRA QA Officer will coordinate data validation and will release the analytical data

How will the data be reported?

Field parameters will be available from surface water quality monitoring and groundwater monitoring immediately after completion of field activities Soil sampling data will be reported by the laboratory upon availability and validated data will be presented in the final summary report Groundwater monitoring data will be reported by the laboratory upon availability and validated data will be presented in the final summary report

How will the data be archived?

Validated data will be archived in an appropriate database to ensure that information is readily available searchable and compatible with a GIS system

QAPP Worksheet #11-6
Project Quality Objectives/Systematic Planning Process Statements
12th Street Landfill Remedial Action Work Plan

Who will use the data?

Weyerhaeuser CRA and the overseeing agencies including the U S EPA and the MDEQ will use the data

What will the data be used for?

The data will be used for the following purposes

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

Confirmation of removal of paper residuals from the wetland north of landfill in accordance with the RA activities required by the ROD

Asphalt Plant Property

Confirmation and documentation of completion of the excavation activities at the asphalt plant property in accordance with the RA activities required by the ROD

MDNR Properties

Confirmation and documentation of completion of the excavation activities at the MDNR property in accordance with the RA activities required by the ROD

What types of data are needed (target analytes, analytical groups field screening on-site analytical or off site laboratory techniques, sampling techniques)?

The data will be used for the following purposes

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

Field screening will rely on the presence of visible residuals The extent of excavation will be determined based on the visual confirmation and no soil sample will be collected.

Asphalt Plant Property

The data will be used to confirm the extent of excavation. Field screening will rely on the presence of visible residuals Confirmatory soil sampling will be assessed by sampling for TCL VOCs and total PCBs using off site analytical testing in a quick turn analysis (i e 24-hours)

MDNR Properties

The data will be used to confirm the extent of excavation. Confirmatory soil sampling will be assessed by sampling for total PCBs using off site analytical testing in a quick turn analysis (i.e 24-hours)

Landfill Grading

- Completion of sampling is through global slope stability modeling

Landfill Gas Management

A modified Tier 3 testing program will (based on the U S EPA s Method 2E) will be implemented to obtain site-specific information regarding potential landfill gas generation and gas quality

QAPP Worksheet #11 6
Project Quality Objectives/Systematic Planning Process Statements
12th Street Landfill Remedial Action Work Plan

How "good" do the data need to be in order to support the environmental decision?

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

The extent of excavation will be determined based on the visual confirmation on site and no verification soil sample will be collected

Asphalt Plant Property

The soil will be analyzed for TCL VOCs and total PCBs in accordance with the performance standards of EPA Methods

MDNR Properties

The soil samples will be analyzed for total PCBs in accordance with the performance standards of EPA Methods

How much data are needed (number of samples for each analytical group matrix and concentration)?

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

The extent of excavation will be determined based on the visual confirmation on site and no verification soil sample will be collected

Asphalt Plant Property

Approximately 13 verification soil samples will be collected. The actual number of samples to be collected on each will be determined following the exaction activities and will be adjusted to meet the MDEQ s Sampling Strategies and Statistic Training Material Part 201 Cleanup Criteria (S3TM)

MDNR Properties

Approximately nine verification soil samples will be collected. The actual number of samples to be collected on each will be determined following the exaction activities and will be adjusted to meet the MDEQ s S3TM guidance

Where, when and how should the data be collected/generated?

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

The extent of excavation will be determined based on the visual confirmation on site and no verification soil sample will be collected

Asphalt Plant Property

The soil samples will be collected from the base of the excavated and surface area of the sidewalls of the excavation from the top 6 inches of native soil below the surface of the exaction base and the sidewalls using a stainless-steel trowel and standard soil sampling and decontamination procedure The excavation and soil sampling activities will be performed according to the RA Work Plan schedule provided to U S EPA

MDNR Properties

The soil samples will be collected from the base of the excavated and surface area of the sidewalls of the excavation from the top 6 inches of native soil below the surface of the exaction base and the sidewalls using a stainless-steel trowel and standard soil sampling and decontamination procedure The excavation and soil sampling activities will be performed according to the RA Work Plan schedule provided to U S EPA

Who will collect and generate the data?

CRA field personnel will collect the samples and generate the field data and sample key the laboratories (WATS and CAS) will analyze the collected field samples and issue data reports and CRA QA Officer will coordinate data validation and release the analytical data

QAPP Worksheet #11-6
Project Quality Objectives/Systematic Planning Process Statements
12th Street Landfill Remedial Action Work Plan

How will the data be reported? Soil sampling data will be reported by the laboratory upon availability in a quick turn analysis (i e 24 to 72 hours) and validated data will be presented to determine the extent of the excavation
How will the data be archived? Validated data will be archived in an appropriate database to ensure that information is readily available searchable and compatible with a GIS system

QAPP Worksheet #12-1
Measurement Performance Criteria (PCBs Surface Water)

Matrix Aqueous
Analytical Group PCBs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A) OR BOTH (S&A)
F 16	W 1	Precision Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Accuracy/Bias	% Recovery (%R) laboratory generated limits[3]	Surrogate	A
		Accuracy/Bias Contamination	< Reporting limit (RL)	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R laboratory generated limits[ ]	Laboratory control sample (LCS)	A
		Accuracy/Bias and Precision	Retention times see analytical SOP	Retention time windows	A
		Accuracy/Bias	%R, same as LCS[ ]	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, same as LCS[ ]	Matrix spike duplicate (MSD) or laboratory control sample duplicate (LCSD)[3]	A
		Precision	RPD <20%	MS/MSD or LCS/LCSD[3]	A

QAPP Worksheet #12-1
Measurement Performance Criteria (PCBs Surface Water)

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field Sampling Plan for sampling procedures
(2) Reference number from QAPP Worksheet #23
(3) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1 1 and 1 2
RPD = relative percent difference

QAPP Worksheet #12-2
Measurement Performance Criteria (Wet Chemistry Surface Water)

Matrix Water

Analytical Group Wet chemistry

Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F 16	W 2 W 3 W 5 W 26	Precision Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration preparation)	S&A
		Accuracy/Bias	%R (90-110)	Continuing calibration verification	A
		Accuracy/Bias	%R (75 125)	MS[3]	A
		Accuracy/Bias	%R (75 125)	MSD[3]	A
		Precision	%R < 20%	MS/MSD[3]	A
		Accuracy/Bias	%R laboratory generated limit[*]	LCS	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) MS and MSD not applicable for TSS

(*) See Attachment 1 1

QAPP Worksheet #12-3
Measurement Performance Criteria (PCBs - Soil/Sediment)

Matrix Soil/Sediment
Analytical Group [1] PCBs
Concentration Level All

SAMPLING PROCEDURE[2]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-4 F 5 F-6	W-4	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias	%R, laboratory generated limits( )	Surrogate	A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment method)	S&A
		Accuracy/Bias	%R, laboratory generated limits(*)	LCS	A
		Accuracy/Bias and Precision	Retention times see analytical SOP	Retention time windows	A
		Accuracy/Bias	%R, same as LCS( )	MS[3]	A
		Accuracy/Bias	%R, same as LCS( )	MSD or LCSD[3]	A
		Precision	%RPD <35%	MS/MSD or LCS/LCSD[3]	A

QAPP Worksheet #12-3
Measurement Performance Criteria (PCBs - Soil/Sediment)

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1 1 and 1 2

QAPP Worksheet #12-4
Measurement Performance Criteria (PCBs – Free Product)

Matrix Free Product
Analytical Group PCBs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A) OR BOTH (S&A)
F 8	C 13 C-14 C 15	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias	%R, laboratory generated limits[*]	Surrogate	A
		Accuracy/Bias Contamination	< 2 x MDL	Blanks (field, equipment method)	S&A
		Accuracy/Bias	%R, laboratory generated limits[*]	LCS	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits[*]	MSD or LCSD[4]	A
		Precision	RPD <30%	MS/MSD or LCS/LCSD[4]	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied

(*) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12-5
Measurement Performance Criteria (TAL Metals – Groundwater / SPLP Metals-Soil)

Matrix Aqueous
Analytical Group TAL Metals / SPLP Metals
Concentration Level All (Except Low Level Mercury)

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F 8 F 11 F 5 F 6	W 14	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits( )	LCS	A
		Precision	sample > 5 x QL RPD ≤ 20% sample ≤ 5 x QL No limit	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory generated limits( )	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits( )	MSD or LCSD[4]	A
		Precision	RPD <20%	MS/MSD or LCS/LCSD[4]	A
		Accuracy	%R > 80%	Interference check sample	A
		Accuracy	RPD ≤ 10%	Serial dilution	A

Footnotes
(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures
(2) Reference number from QAPP Worksheet #23
(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.
(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1 1
RPD = relative percent difference

QAPP Worksheet #12-6
Measurement Performance Criteria (TAL Metals-Soil)

Matrix Soil
Analytical Group TAL Metals
Concentration Level All (Except Low Level Mercury)

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A), OR BOTH (S&A)
F 5 F 6	W 14	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment method)	S&A
		Accuracy/Bias	%R, laboratory generated limits(*)	LCS	A
		Precision	sample > 5 x QL RPD ≤ 20% sample ≤ 5 x QL No limit	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory generated limits( )	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits( )	MSD or LCSD[4]	A
		Precision	%RPD <40%	MS/MSD or LCS/LCSD[4]	A
		Accuracy	%R > 80%	Interference check sample	A
		Accuracy	RPD ≤ 10%	Serial dilution	A

Footnotes
(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures
(2) Reference number from QAPP Worksheet #23
(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.
(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.
( ) See Attachments 1 1
RPD = relative percent difference

QAPP Worksheet #12-7
Measurement Performance Criteria (Cyanide - Groundwater)

Matrix Aqueous
Analytical Group Cyanide
Concentration Level All total

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A), OR BOTH (S&A)
F 8 F 11	W 24	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits	LCS	A
		Precision	%RPD <20%	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory generated limits( )	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits( )	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1 1

RPD = relative percent difference

QAPP Worksheet #12-8
Measurement Performance Criteria (Cyanide - Soil)

Matrix Soil
Analytical Group Cyanide
Concentration Level All total

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A) OR BOTH (S&A)
F 5 F-6	W 25	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment method)	S&A
		Accuracy/Bias	%R, laboratory generated limits	LCS	A
		Precision	%RPD <20%	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory generated limits(*)	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits(*)	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A

Footnotes
(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures
(2) Reference number from QAPP Worksheet #23
(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated
(4) MS and MSD must be client provided LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1 1
RPD = relative percent difference

QAPP Worksheet #12 9
Measurement Performance Criteria (Low-Level Mercury and Methyl Mercury Groundwater)

Matrix Aqueous
Analytical Group Mercury
Concentration Level Low Level

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A), OR BOTH (S&A)
F 8 F 11	C-4 C 7	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits( )	LCS	A
		Precision	RPD	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits( )	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits( )	MSD or LCSD[4]	A
		Precision	%RPD <24%	MS/MSD or LCS/LCSD[4]	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated

(4) MS and MSD must be client provided LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1 1

RPD = relative percent difference

QAPP Worksheet #12 10
Measurement Performance Criteria (SVOCs - Groundwater)

Matrix Aqueous
Analytical Group SVOCs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F 8 F 11	W 15	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, Laboratory generated limits[*]	LCS	A
		Accuracy/Bias	%R, Laboratory generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, Laboratory generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, Laboratory generated limits[*]	Surrogates	A
		Accuracy/Bias	+100% 50% of ICAL	Internal standards	A
		Accuracy/Bias	Established mass limits	DFTPP Tuning	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12-11
Measurement Performance Criteria (SVOCs Soil)

Matrix Soil
Analytical Group SVOCs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A), OR BOTH (S&A)
F 5 F 6	W 15	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, Laboratory generated limits[*]	LCS	A
		Accuracy/Bias	%R, Laboratory generated limits[ ]	MS[4]	A
		Accuracy/Bias	%R, Laboratory generated limits[ ]	MSD or LCSD[4]	A
		Precision	%RPD <40%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, Laboratory generated limits[ ]	Surrogates	A
		Accuracy/Bias	+100% 50% of ICAL	Internal standards	A
		Accuracy/Bias	Established mass limits	DFTPP Tuning	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12 12
Measurement Performance Criteria (VOCs - Groundwater)

Matrix Aqueous
Analytical Group VOCs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A) OR BOTH (S&A)
F 8 F 11	W 21	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits[*]	LCS	A
		Accuracy/Bias	%R, laboratory generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, laboratory generated limits[*]	Surrogates	A
		Accuracy/Bias	+100% 50% of ICAL	Internal standards	A
		Accuracy/Bias	Established mass limits	BFB Tuning	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated

(4) *MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.*

(*) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12-13
Measurement Performance Criteria (VOCs Soil)

Matrix Soil
Analytical Group VOCs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A), OR BOTH (S&A)
F 5 F 6	C-5	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits[*]	LCS	A
		Accuracy/Bias	%R, laboratory generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <40%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, laboratory generated limits[*]	Surrogates	A
		Accuracy/Bias	Established mass limits	BFB Tuning	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied

(*) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12-14
Measurement Performance Criteria (DRO & GRO Soil)

Matrix Soil
Analytical Group DRO, GRO
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F 5 F 6	W 22 (DRO)	Precision-Overall	RPD < 100%	Field duplicate	S&A
	W 23 (GRO)	Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, Laboratory generated limits	LCS	A
		Accuracy/Bias	%R, Laboratory generated limits (50% 150%)	MS	A
		Accuracy/Bias	%R, laboratory generated limits(*)	MSD or LCSD[4]	A
		Precision	%RPD <10%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, Laboratory generated limits(*)	Surrogate	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12-15
Measurement Performance Criteria (Wet Chemistry – Soil)

Matrix Soil

Analytical Group Wet chemistry

Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S) ANALYTICAL(A), OR BOTH (S&A)
F 5 F-6	C 8 C 9 and C 10	Precision Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration preparation)	S&A
		Accuracy/Bias	%R laboratory generated limit( )	Continuing calibration verification	A
		Accuracy/Bias	%R laboratory generated limit( )	MS[3]	A
		Accuracy/Bias	%R laboratory generated limit( )	MSD[3]	A
		Precision	%R laboratory generated limit( )	MS/MSD[3]	A
		Accuracy/Bias	%R laboratory generated limit( )	LCS	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) MS and MSD not applicable for Nitrogen compounds (Ammonia N Nitrate and Nitrite) and phosphorous

(*) See Attachment 1 1

QAPP Worksheet #12-16
Measurement Performance Criteria (Low-Level Mercury and Methyl Mercury – Surface Water)

Matrix Aqueous
Analytical Group Mercury
Concentration Level Low Level

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F 16	C-4 C 7	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits( )	LCS	A
		Precision	RPD laboratory generated limits	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits( )	MS[4]	A
		Accuracy/Bias	%R, laboratory generated limits( )	MSD or LCSD[4]	A
		Precision	%R, laboratory-generated limits( )	MS/MSD or LCS/LCSD[4]	A

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project specific Field Sampling Plan for sampling procedures

(2) Reference number from QAPP Worksheet #23

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.

( ) See Attachments 1 1 and 1 2

RPD = relative percent difference

QAPP Worksheet #12-17
Measurement Performance Criteria (PCBs Groundwater)

Matrix Aqueous
Analytical Group PCBs
Concentration Level All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A) OR BOTH (S&A)
F 3 F 11 F 16	W 1	Precision Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Accuracy/Bias	% Recovery (%R) laboratory generated limits[3]	Surrogate	A
		Accuracy/Bias Contamination	< Reporting limit (RL)	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R laboratory generated limits[ ]	Laboratory control sample (LCS)	A
		Accuracy/Bias and Precision	Retention times see analytical SOP	Retention time windows	A
		Accuracy/Bias	%R, same as LCS[ ]	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, same as LCS[ ]	Matrix spike duplicate (MSD) or laboratory control sample duplicate (LCSD)[3]	A
		Precision	RPD <20%	MS/MSD or LCS/LCSD[3]	A

QAPP Worksheet #12-17
Measurement Performance Criteria (PCBs - Groundwater)

Footnotes

(1) Reference number from QAPP Worksheet #21 See the project-specific Field Sampling Plan for sampling procedures
(2) Reference number from QAPP Worksheet #23
(3) MS and MSD must be client provided. LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1 1 and 1 2
RPD = relative percent difference

QAPP Worksheet #13-1
Secondary Data Criteria and Limitations
12th Street Landfill RA Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/ collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Soil and residuals sampling data	June and Sept. 1987 and January 1989 MDNR and Mill Staff 24 soil and residual samples outside berm (Discussed in G&M 1994a)	Plainwell Paper Co KRSG	Remedial design	U S EPA approval
Electromagnetic conductivity and magnetometer survey data	G&M, 1991 "12th Street Landfill Geophysical Investigation, Plainwell Michigan." Letter Report by Geraghty and Miller Inc October 11 1991	Plainwell Paper Co KRSG	Remedial design	U S EPA approval
Soil and residuals sampling data	G&M 1994a 'Test Pit Investigation, Technical Memorandum, 12th Street Landfill Operable Unit, Plainwell Michigan, Allied Paper Inc./Portage Creek/Kalamazoo River Superfund Site Geraghty and Miller Inc February 18 1994	Plainwell Paper Co KRSG	Remedial design	U S EPA approval
Sediment probing data, soil and residuals sampling data, groundwater sampling data	G&M, 1994b Allied Paper Inc./Portage Creek/Kalamazoo River Superfund site Remedial Investigation/Feasibility Study Technical Memorandum 8 12th Street Landfill Operable Unit, Plainwell Michigan. May 31 1994	Plainwell Paper Co KRSG	Site characterization	U S EPA approval(1)
Groundwater sampling data	G&M, 1996a. Remedial Investigation Addendum I 12th Street Landfill Operable Unit, Plainwell Michigan, Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site " March 26, 1996	Plainwell Paper Co KRSG	Remedial design	U S EPA approval
Summary of existing data residuals sampling data	G&M, 1996b "Remedial Investigation Report, 12th Street Landfill Operable Unit, Plainwell Michigan, Allied Paper Inc /Portage Creek/Kalamazoo River Superfund Site " Geraghty and Miller, Inc December 20, 1996	Plainwell Paper Co KRSG	Remedial design	U S EPA approval

QAPP Worksheet #13-1
Secondary Data Criteria and Limitations
12th Street Landfill RA Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/ collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Geotechnical data	BBL, 2001a. "Geotechnical Sample Analytical Data, 12th Street Landfill Operable Unit Transmittal Letter with Attachments Blasland, Bouck & Lee Inc June 25, 2001	KRSG	Remedial design	U S EPA approval
Sediment probing data	BBL 2001b as reported in final data summary report soil/sediment sampling results pre design sampling 12th Street Landfill, Operable Unit #4 Allied Paper Inc /Portage Creek/Kalamazoo River Site Plainwell Michigan July 2004	KRSG	Site characterization	U S EPA approval(1)
Wetland delineation	CDM, 2002 "Michigan Department of Environmental Quality Kalamazoo River and Portage Creek Wetland Delineation Study " Camp Dresser and McKee January 2002	MDEQ	Remedial design	U S EPA approval
Sediment probing data	U S EPA, 2004 Final data summary report soil/sediment sampling results pre-design sampling 12th Street Landfill Operable Unit #4 Allied Paper Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan. July 2004	U S EPA	Site characterization	U S EPA approval(1)
Wastewater treatment system discharge surface water and residual data	RMT Inc 2007 Emergency Response Plan Design Report, 12th Street Landfill Operable Unit #4 Allied Paper Inc /Portage Creek/Kalamazoo River Site, Plainwell, Michigan. July 2007	RMT	Site characterization	U S EPA approval
Summary of existing data including protective determination	U S EPA, 2007 First Five Year Review Report Final, 12th Street Landfill, Operable Unit #4 Allied Paper Inc./Portage Creek/Kalamazoo River Site Plainwell, Michigan, October 2007	U.S EPA	Site characterization	U S EPA approval

QAPP Worksheet #13 1
Secondary Data Criteria and Limitations
12th Street Landfill RA Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/ collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Soil and paper residual sampling data	RMT Inc 2008 Remedial Design Work Plan report soil/residual sampling results pre-design sampling 12th Street Landfill, Operable Unit #4 Allied Paper Inc./Portage Creek/Kalamazoo River Site Plainwell Michigan June 2008	RMT	Remedial Design	U S EPA approval
Pre final design investigation	RMT Inc 2008 Remedial Design Work Plan report soil/residual sampling results pre-design sampling 12th Street Landfill Operable Unit #4 Allied Paper Inc./Portage Creek/Kalamazoo River Site, Plainwell Michigan June 2008	RMT	Remedial Design	U S EPA approval

Footnote.

(1) Data and observations collected during the sediment excavation will take precedence

QAPP Worksheet #13 2
Secondary Data Criteria and Limitations
Plainwell Mill Phase II RI Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Sediment coring observations and survey results	RMT July 2007 Visual Assessment of the Plainwell Mill Banks	RMT July 2007	Site Characterization	U S EPA approval[1]
Prior investigations	BBL 1996 Technical Memorandum 15 Mill Investigations	BBL 1996	Site Characterization	Data are historical and site conditions may have changed
	ERM, 1997 Simpson Plainwell Paper Company Phase I environmental site assessment and Phase II investigation, Plainwell Michigan	ERM 1997		
	Plainwell Paper 1999 & 2000 Letter to Michigan Department of Environmental Quality	Simpson Plainwell Oil spill clean up samples 1999 & 2000		
	CDM 2001 Plainwell Paper Gray Seam Investigation.	CDM October 2001		
	Weston, 2002 Removal Assessment Report for Allied Paper – Kalamazoo River Site Otsego/Plainwell	Weston July and August 2001		
	BBL 2003 PCB Data for the Plainwell Impoundment River Bank Soil Samples	BBL October 2003		
	FTCH, 2006 Phase II Environmental Site Assessment, Former Plainwell Paper Mill	FTCH October 2006		
	RMT 2008 Plainwell Mill Banks Emergency Action Documentation Report.	RMT January 2009		
	RMT 2006 Draft RI/FS Work Plan Report, September 2006	RMT Document not finalized		

QAPP Worksheet #13 2
Secondary Data Criteria and Limitations
Plainwell Mill Phase II RI Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
	RMT 2009 Phase 1 Plainwell Mill RI/FS Work Plan. Summary of Test Pit Activities and Results for Plainwell Mill technical memorandum January 2009	RMT January 2009		
	RMT 2009 Phase 1 Plainwell Mill RI/FS Work Plan. Initial Groundwater and Coal Tunnel Assessment Work Plan technical memorandum, February 2009	RMT February 2009		

Footnote
(1) Data and observations collected during the sediment excavation will take precedence

QAPP Worksheet #14
Summary of Project Tasks

SAMPLING AND ANALYSIS TASKS	
Emergency Response Activities in the Former Powerhouse Discharge Channel at the 12th Street Landfill (Operable Unit No 4)	
Sampling tasks	Sampling tasks will be performed as follows • Pre-excavation bathymetry measurements and sediment sampling to plan extent of sediment excavation (*i e* analytical data for polychlorinated biphenyls (PCBs) visual characterization and engineering data) • Resuspension monitoring and control, including surface water sampling and field turbidity measurements • Dewatering system discharge monitoring • Post excavation confirmation sampling for PCBs in channel sediment • Global positioning system (GPS)–based survey of excavation limits and sampling locations • Digital photographs

Analysis tasks	Analytical samples will be processed, prepared, and analyzed, as follows
	• Resuspension monitoring and control (surface water)
	  • PCBs by WATS
	• Dewatering system discharge monitoring (surface water)
	  • PCBs total suspended solids (TSS) and phosphorus by WATS
	• Post excavation confirmation sampling (sediment)
	  • PCBs by WATS

Quality control tasks	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1 5) QA samples will be collected as described in Worksheet #26
Secondary data	See Worksheets #13 1 and #13 2

QAPP Worksheet #14
Summary of Project Tasks

SAMPLING AND ANALYSIS TASKS	
Predesign Investigations for the Remedial Design for the 12th Street Landfill (Operable Unit No 4)	
Sampling tasks	Field data collection activities during the predesign investigations will include • Visual information obtained by the advancement of test pits • Visual information obtained by the advancement of Geoprobe® borings • Gas concentrations (methane carbon dioxide and oxygen) measured in existing monitoring wells and in the Geoprobe® locations Pressure measured in existing monitoring wells
Analysis tasks	No analytical data will be collected.
Quality control tasks	No analytical data will be collected.
Secondary data	See Worksheet #13 1
Phase 2 of Addendum No 1 – Test Pits & Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment	
Sampling tasks	Sampling tasks will be performed as follows **Phase 2 of Addendum No 1** Approximately 15 test pits will be excavated along the banks of the Plainwell Mill buildings • Test pit excavation to determine extent of oil impacted soil and elevated concentrations of PCBs (*i e* analytical data for polychlorinated biphenyls (PCBs) & total petroleum hydrocarbons visual characterization, and engineering data) • Additional soil samples will be collected from the test pits for RCRA metals VOCs and PAHs • If free product is observed a sample will be collected for general characteristics • Global positioning system (GPS)–based survey of excavation limits and sampling locations • Digital photographs **Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment** Approximately 12 groundwater wells and three staff gages will be installed. • Collect groundwater samples for RCRA metals VOCs PAHs and PCBs • Collect water elevations from three surface water staff gages (Two in the Kalamazoo River and One in the Mill Race) • Global positioning system (GPS)–based survey of excavation limits and sampling locations • Digital photographs

QAPP Worksheet #14
Summary of Project Tasks

Analysis tasks	Analytical samples will be processed, prepared, and analyzed, as follows **Phase 2 of Addendum No 1 Test Pits Soil Samples** • PCBs by WATS • RCRA Metals by WATS • PAHs by WATS • VOCs by Columbia Analytical Services • Free Product Characterization (Specific Gravity & Viscosity) – Summit Technologies Inc • Total petroleum hydrocarbons (DRO/GRO) by WATS **Plainwell Mill RI/FS – Initial Groundwater Assessment (Groundwater Samples)** • PCBs by WATS • RCRA Metals by WATS • Hg by Columbia Analytical Services • PAHs by WATS • VOCs by Columbia Analytical Services
Quality control tasks	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1 5) QA samples will be collected as described in Worksheet #26
Secondary data	See Worksheets #13 1 and #13 2
SAMPLING AND ANALYSIS TASKS	
Plainwell Mill Phase II Remedial Investigation Work Plan	
Sampling tasks	Sampling tasks will be performed as follows • Advancement of soil boring and performing soil sampling as described in Worksheet# 18 5 • Installation of monitoring wells at various location at the site • Performance of side-wide groundwater monitoring at existing and new monitoring locations • GPS–based survey of soil boring and groundwater monitoring locations • Collection of two surface water samples one from millrace and one from Kalamazoo River • Digital photographs

QAPP Worksheet #14
Summary of Project Tasks

Analysis tasks	Analytical samples will be processed, prepared, and analyzed, as follows
	• Surface water sampling
	  • Low level mercury methyl mercury by CAS and
	  • hardness by WATS
	• Soil sampling
	  • TCL SVOCs TAL Metals SPLP Metals and PCBs by WATS
	  • TCL VOCs and general chemistry by CAS
	• Groundwater monitoring
	  • TCL VOCs by WATS
	  • TCL SVOCs, PCBs, and TAL inorganics by WATS

Quality control tasks	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1 5) QA samples will be collected as described in Worksheet #26
Secondary data	See Worksheets #13 1 and #13 2
12th Street Landfill Remedial Action Work Plan	
Sampling tasks	Sampling tasks will be performed as follows • Asphalt Plant Property • Post excavation soil sampling at the base of excavation and sidewalls of the excavated area. • GPS–based survey of excavation limits and sampling locations • Digital photographs • MDNR Property • Post excavation soil sampling at the base of excavation and sidewalls of the excavated area • GPS–based survey of excavation limits and sampling locations • Digital photographs

QAPP Worksheet #14
Summary of Project Tasks

Analysis tasks	Analytical samples will be processed, prepared, and analyzed, as follows
	• Soil samples collected from Asphalt Plant Property
	  • PCBs by WATS
	Soil sampling collected from MDNR Property
	  • TCL VOCs by CAS
	  • PCBs by WATS

Quality control tasks	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1 5) QA samples will be collected as described in Worksheet #26
Secondary data	See Worksheets #13 1 and #13 2
DATA MANAGEMENT DOCUMENTATION RECORDS, AND AUDIT TASKS	

Data management tasks	• **Field data reduction** Raw data from field measurements and sample collection activities will be recorded as specified in the FSP If the data are to be used in the project reports they will be reduced or summarized, and the method of reduction will be documented in the report. With the exception of the temperature correction for specific conductance no calculation will be involved in field data reduction. Only direct reading instrumentation will be employed in the field. The On Site Coordinator or designee will proofread all forms and notebooks to determine if transcription errors have been made by the field crew
	• **Laboratory data reduction** WATS or subcontracted laboratory (i e CAS) will perform in house analytical data reduction under the direction of the laboratory QA/QC Manager The laboratory QA/QC Manager will be responsible for assessing data quality and advising of any data that were rated "preliminary or 'unacceptable or of other notations that would caution the data user of possible unreliability Data reduction, by the laboratory will be conducted as follows
	  • The analysts who produced the laboratory data will first conduct a systematic review (Level 1 Review)
	  • An experienced peer supervisor or designee will examine the data (the Level 2 Review) to ensure that the Level 1 review has been completed correctly and thoroughly Following the Level 2 review the data will be turned over to the Laboratory Project Manager for a third level review
	  • The Project Manager will review the data for completeness and attainment of quality control criteria as outlined in the U S EPA methods and for overall reasonableness
	  • The Project Manager will verify the accuracy and completeness of the final reports
	  • The Laboratory QA/QC Manager and the supervisor of the pertinent analytical section, in conjunction with the CRA QA Officer will decide whether any sample reanalysis is required.
	  • Data reduction procedures are included in the U S EPA approved methods and associated laboratory SOPs
	• **Field data reporting** Field data reporting will consist of field logs and calibration and measurement records documenting site activities as described in the FSP and on the sample Chain of-Custody (COC) Records

QAPP Worksheet #14
Summary of Project Tasks

Data management tasks (*continued*)	• **Laboratory data reporting** The analytical laboratories will prepare and retain full analytical and QC documentation Such retained documentation need not be on hard (paper) copy but may be in other storage media (*e g* computer diskette or magnetic tape) As needed, WATS or subcontractor laboratory (i e CAS) will supply a hard copy of the retained information WATS or subcontractor laboratory (i e CAS) will provide the following information in each analytical data package submitted • Dated cover sheets signed by the WATS or subcontractor laboratory (i e CAS) Laboratory Manager listing a laboratory batch number the analyses performed, the number of samples and respective matrices the project name and number narrative comments describing deviations from intended analytical strategy and any problems encountered in analysis a discussion of any laboratory quality control checks that failed to meet project criteria and the signature of the laboratory QA/QC Manager • Tabulated results of inorganic and organic compounds identified and quantified, including sample preparation and analysis dates, and cross references of laboratory and field sample identification numbers • Analytical results for QC sample spikes and sample duplicates initial and continuing calibration verifications of standards and blanks standard procedural blanks laboratory control samples and the data produced by ICP interference check samples as appropriate for the specified analyses • Tabulation of Method Detection Limits as appropriate • Raw data system printouts (or legible photocopies) identifying the date of analyses the mass spectra tuning data, the name of the analyst, the parameters determined, the initial and continuing calibration, the calibration verification summary the method blanks the sample and any dilutions sample duplicates and spikes chromatograms GC/MS spectra, computer printouts internal standard area and RT summary cleanup information, control samples ICP outputs and inter-element correction data WATS or subcontractor laboratory (i e CAS) will provide the following information for the indicator parameters in each analytical data package submitted • Dated cover sheets listing a laboratory batch number the analyses performed, the number of samples and respective matrices project name and number narrative comments describing deviations from intended analytical strategy and problems encountered in analysis discussion of any laboratory quality control checks that failed to meet project criteria and the signature of the Laboratory QA Manager • Copies of bench sheets that include summaries of initial calibration and continuing calibration check results • Summary of QC sample analysis (spikes duplicates laboratory control samples and blanks) A report will be prepared containing a QA/QC section summarizing the quality of the data. The QA report prepared by the CRA will address the assessment of data precision, accuracy completeness and comparability the results of performance audits if any the results of system audits any reported nonconformances any significant QA/QC problems and recommended solutions the results of corrective actions since the last report and approved revisions to the QA/QC processes The report will indicate whether the QA objectives were met and whether the data can be used for the intended purposes based on an evaluation of compliance with control limits the results of audits and compliance with the procedures specified in the QAPP and the FSP

QAPP Worksheet #14
Summary of Project Tasks

Documentation and records	Appropriate records will be maintained to provide adequate documentation of the entire data generation process including field sampling and laboratory analysis • **Field documentation** Field personnel will develop and retain comprehensive records of field activities, including field sampling, field analysis, and sample COC Record, to allow a reconstruction of field events and sample handing during data review and interpretation. • **Laboratory project files** WATS or subcontractor laboratory (i.e CAS) will maintain a file for pertinent project information, including COC Records other custody documents (air bills etc) work orders Sample Receipt Acknowledgment Forms if any instrument detection limit and control limit tabulations all raw analytical data on bench sheets laboratory data and project communication records Such retained documentation need not be on hard (paper) copy but may be in other storage media (*e g* computer diskette or magnetic tape) As needed, WATS or subcontractor laboratory (i e CAS) will supply a hard copy of the retained information • **Laboratory notebooks** Logbooks, bench sheets, instrument notebooks and instrument printouts will be retained as part of the permanent laboratory record, including the associated quality controls Each page in the laboratory logbooks and bench sheets will be signed and dated by the analyst, and errors will be crossed out in indelible ink System printouts of raw inorganic and organic data will include dates of analyses analyst s name parameters determined, calibration curve calibration verifications method blanks sample number and dilutions performed, and sample duplicates spikes and control samples Internal laboratory QC sample results will be indicated on the analytical bench sheets and will include sample spikes sample duplicates initial and continuous calibration verification of standards and blanks standard procedural blanks laboratory control samples ICP serial dilutions and ICP interference check samples • **Computer and hard copy storage** All electronic files and deliverables will be retained by the laboratory for no less than 5 years Weyerhaeuser or its designated representatives will retain copies of the analytical data reports according to the requirements of the laboratory QA Manual All field records will be kept in the central project file at the CRA offices at St Catharines Waterloo or Kalamazoo and records will be included in project reports as appropriate or upon request by the U S EPA RPM • **Field data reporting** Field data reporting will consist of field notebooks and logs photographs, boring logs calibration and measurement records and COC documentation, including field quality control samples that will be collected to assess the quality of the analytical data and to evaluate sampling and analytical reproducibility Field records will be reviewed by the CRA Project Manager for consistency with the planned activities, and any concerns will be discussed with the Field QA Officer Field performance and field system audits will also be performed, as discussed below and in Worksheets #31 and 32 • **Laboratory data reporting** Analytical data for this project will be reported in both an electronic data deliverable (EDD) and an analytical data package The EDD will be generated by WATS or subcontractor laboratory (i e CAS) and will be used by CRA to facilitate loading the analytical data into the project database The Laboratory QA/QC Manager will perform a final review of the report summaries and case narratives to determine if the report meets project requirements The task of reporting laboratory data to the U S EPA will begin after the data review activity has been concluded. The validated analytical data will be provided to the U S EPA in accordance with the project schedule (Worksheet #16) In addition to the COC Record, WATS or subcontractor laboratory (i e CAS) will prepare and provide a full 'CLP like data package including the following

QAPP Worksheet #14
Summary of Project Tasks

Documentation and records (*continued*)	• **Case narrative** date of issuance laboratory analysis performed any deviations from required analytical methods laboratory sample lot numbers numbers of samples and respective matrices QC procedures used and references to the acceptance criteria, laboratory report table of contents project name and number condition of samples upon receipt, dates of extraction, preparation, and analysis discussion of whether or not sample holding times were met discussion of technical problems or other observations that may have created analytical difficulties discussion of any laboratory QC checks that failed to meet project criteria, signature of the laboratory Project Manager and copies of the COC Records • **Chemistry data package** run log summary page indicating dates of analyses for samples and laboratory QC checks cross referencing of laboratory sample to project sample identification numbers, adequately described data qualifiers sample preparation and analysis methods sample results matrix spike and matrix spike duplicate (MS/MSD) recoveries laboratory control sample recoveries, method blank results and surrogate recoveries Soil sample analytical data generated by the laboratory will be reported in micrograms per kilogram (µg/kg) on a dry weight basis Groundwater data will be reported in micrograms per liter (µg/L) Results between the laboratory Method Detection Limit (MDL) and the Quantitation Limit (QL) will be reported. Data retained in the project database may be converted to units other than those reported by the laboratories Sample results will not be corrected for contamination found in laboratory blanks However sample results may be qualified as not detected based on laboratory field, and/or trip blank contamination. WATS or subcontractor laboratory (i e CAS) will provide the following information in each analytical data package submitted • Dated cover sheets signed by the WATS or subcontractor laboratory (i e CAS) Laboratory Manager listing a laboratory batch number the analyses performed, the number of samples and the respective matrices the project name and number narrative comments describing deviations from intended analytical strategy and problems encountered in analysis a discussion of any laboratory quality control checks that failed to meet project criteria, and the signature of the laboratory QA Manager • Tabulated results of inorganic and organic compounds identified and quantified, including sample preparation and analysis dates and cross references of laboratory and field sample identification numbers • Analytical results for QC sample spikes sample duplicates and blanks initial and continuing calibration verifications of standards and blanks standard procedural blanks laboratory control samples and the data produced by inductively coupled plasma (ICP) interference check samples as appropriate for the specified analyses • Tabulation of Method Detection Limits as appropriate • Raw data system printouts (or legible photocopies) identifying dates of analyses mass spectra tuning data, name of analyst, parameters determined, initial and continuing calibration calibration verification summary method blanks sample and any dilutions sample duplicates and spikes chromatograms gas chromatograph/mass spectrophotometer (GC/MS) spectra, computer printouts internal standard area and retention time (RT) summary cleanup information, control sample results ICP outputs and inter-element correction data

QAPP Worksheet #14
Summary of Project Tasks

Assessment/Audit tasks	Performance and system audits will be completed in the field and laboratory as described below and in Worksheets #31 and 32
	• **Field audits** The Project Manager will monitor day to-day field performance through daily communications with the Project Coordinator and on-site field staff and the Construction Manager In addition, field performance audits and field system audits will be performed, as follows
	  • **Field performance audits** Field performance audits will be conducted in order to confirm that the activities are being performed according to the established plans The field performance audit(s) will be performed by the Senior Consultant QA Manager (or her designee) at a frequency that is appropriate for the field activities being performed. The audit(s) will include a discussion of the project progress with the Project Manager and/or the review of field reports as appropriate The Senior Consultant QA Manager will record and document any observations made during field system audits and will discuss the audit and any recommended changes/deviations to the field procedures with the Project Manager
	  • **Field system audits** Field system audits will be performed by the CRA QA Officer including a review of rinse and trip blank data to identify potential deficiencies in field sampling and decontamination procedures and a comparison of the scheduled QA/QC activities described in this QAPP with the QA/QC procedures being performed on the project. Field system audits will be performed at a frequency appropriate for the field activities The CRA QA Officer will record and document any observations made during field system audits and will discuss the audit and any recommended changes/deviations to the field procedures with the Project Manager
	• **Laboratory audits** Laboratory audits will be performed, as follows
	  • **Internal audits** The Laboratory QA/QC Manager (or his designee) will conduct internal laboratory audits periodically This will include an overall evaluation of the performance of laboratory staff and a comparison of laboratory procedures with the laboratory QA Manual and SOPs Results of the audits will be summarized and distributed to appropriate laboratory staff
	  • **External audits** The CRA QA Officer will review the laboratory QA Manual and applicable SOPs and will discuss laboratory procedures with the Laboratory QA/QC Manager prior to the start of project sampling The CRA QA Officer will record and document any observations made during the review In addition, as a participant in state and federal certification programs the laboratory is audited by representatives of the regulatory agency issuing certification Audits include a review of sample handling and tracking documentation, analytical methodologies, analytical supportive documentation, and final reports The audit findings are documented and submitted to the laboratory for corrective action if necessary
	• **Corrective action** Corrective actions are required when field or analytical data are not within the objectives specified in this QAPP as follows

QAPP Worksheet #14
Summary of Project Tasks

Assessment/Audit tasks (*continued*)	• **Field measurement corrective action** Corrective action in the field may be necessary when the sample network is changed (*i e* more/fewer samples sampling locations other than those specified in the FSP etc) or when sampling procedures and/or field analytical procedures require modification in response to unexpected conditions Technical staff and project personnel will be responsible for reporting all suspected technical or QA nonconformances or deficiencies of any activity or issued document by reporting the situation to the CRA Project Coordinator or designee The CRA Project Coordinator will assess the suspected problems in consultation with the CRA Project Manager or CRA QA Officer or designee and will assist in making a decision based on the potential for the situation to impact the data quality If it is determined that the situation warrants a reportable nonconformance requiring corrective action, the CRA Field QA Officer will initiate a nonconformance report. If appropriate the CRA Field QA Officer will ensure that no additional work that is dependent on the nonconforming activity is performed until the corrective actions are completed. • **Laboratory corrective action** Corrective actions are required whenever an out-of-control event or potential out-of control event is noted. Corrective actions may be necessary if any of the following occur· ▪ QC data are outside the warning or acceptable windows for precision and accuracy ▪ Blanks contain target analytes above acceptable levels Undesirable trends are detected in spike recoveries or the RPD between duplicates ▪ There are unusual changes in detection limits ▪ Deficiencies are detected by the Laboratory Manager during internal or external audits or from the results of performance evaluation samples ▪ Inquiries concerning data quality are received. Corrective actions should be timely and they should determine the root cause and evaluate any propagation of the error or problem. The investigative action taken is somewhat dependent on the analysis and the event Corrective action in the laboratory may occur prior to during, or after the initial analysis Corrective action is under the supervision of the Laboratory Manager and Laboratory QA Officer Following a consultation with laboratory scientists technicians and team leaders it may be necessary for the Laboratory Manager to approve the implementation of the corrective action. Some conditions during or after analysis may automatically trigger corrective action or optional procedures These conditions may include dilution of samples additional sample extract cleanup and automatic reinjection/reanalysis when certain quality control criteria are not met, etc WATS or subcontractor laboratory s (i e CAS) corrective action procedures are documented in Laboratory SOPs specifying corrective action to be taken when an analytical error is discovered or the analytical system is found to be out of control

QAPP Worksheet #14
Summary of Project Tasks

Assessment/Audit tasks (*continued*)	Depending on the problem the corrective action employed may be formal or informal On the spot actions are used to correct minor problems such as recalibration, retuning or a minor repair (*e.g* replacement of a minor part) of a malfunctioning instrument or the correction of poor analytical technique being used. Corrective action procedures may be handled at the bench level by the analyst, who reviews the preparation or extraction procedure that was used for possible errors and checks the instrument calibration, spike and calibration mixes and the instrument sensitivity These occurrences are documented in the appropriate injection, run, or analysis logbooks Similarly routine instrument maintenance malfunctions, and power failures are also documented in the appropriate instrument maintenance logbooks If the problem persists or cannot be identified, the matter may be referred to the laboratory team leader and/or QA/QC Manager for further investigation Occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated will be properly documented. The corrective action procedure will be discussed with the Laboratory Project Manager and full documentation of the corrective action procedure whether resolved or not, will be placed in the laboratory project file Corrective actions specific to analytical methods are discussed in the operational specific SOPs The U S EPA RPM or the CRA QA Officer may request corrective action for any nonconformance identified by audits or data validation. • **Corrective action during data validation and data assessment** The need for corrective actions may be identified during data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory Data validation corrective actions may include notification of the laboratory of incomplete or erroneous reports and a request for issuance of corrected versions When the CRA QA Officer identifies a corrective action situation, the CRA Project Manager will approve the implementation of corrective action, including possible resampling. The CRA QA Officer will notify the laboratory of incomplete or erroneous reports and will request the issuance of corrected versions All corrective actions will be documented Final summary data tables will not be issued until all data have been validated and all corrections have been made Corrective action may include the following ▪ Reanalysis of samples if holding time requirements permit ▪ Resampling and analysis ▪ Evaluation and amendment of sampling procedures ▪ Evaluation and amendment of analytical procedures ▪ Acceptance of data and acknowledgment of the level of uncertainty
Data Review tasks	See Worksheets #36 and 37

QAPP Worksheet #15-1
Reference Limits and Evaluation (Surface Water)

ANALYTE	CAS NUMBER	PROJECT ACTION LIMIT[1]	WATER (µg/L)[2]	
			LABORATORY MDL	LABORATORY RL
PCBs (U S EPA 608)[3]				
Aroclor 1016	12674-11 2		0 10	0 2
Aroclor 1221	11104-28 2			0 2
Aroclor 1232	11141 16 5			0 2
Aroclor 1242	53469 21 9	--		0 2
Aroclor 1248	12672 29 6			0 2
Aroclor 1254	11097-69 1			0 2
Aroclor 1260	11096-82 5	--	0 10	0 2
Total PCBs	1336-36-3	0 2 µg/L		0.2
Metals				
Low Level Mercury	7439 97-6		0 08 ng/L	1 ng/L
Methyl Mercury	22967 92-6	--	0 05 ng/L	0 1 ng/L
Inorganics (Wet Chemistry)[4]				
TSS (U S EPA 160 2)	--	30-45 mg/L	--	5 0 mg/L[5]
Total phosphorus as P (U S EPA 365.2)	7723 14-0	--	--	0 01 mg/L
Hardness (SM 2340B)-Calculation of Ca & Mg	14797-65-0	--	0 0033 mg/L	1 66 mg/L

Notes

(1) Standards are consistent with the Multi Area Quality Assurance Project Plan (Rev 00) For the Kalamazoo River Study Group (Arcadis BBL, 2007b) which are from the MDEQ s Substantive Requirements Document for the Plainwell Dam Superfund Site, dated February 13 2007 The TSS standards are on a monthly and daily basis respectively
(2) Concentrations are in µg/L except where noted.
(3) U S EPA *Appendix A to Part 136 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater Method 608—Organochlorine Pesticides and PCBs* July 1995
(4) U S EPA. *Methods for Chemical Analysis of Water and Wastes* EPA/600/4-79/020 EMSL-Cincinnati 1983
(5) The actual Reporting Limit will depend on the volume of sample filtered.

RL = reporting limit
MDL = Method Detection Limit
µg/L = micrograms per liter
mg/L = milligrams per liter
PCBs = polychlorinated biphenyls

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
INORGANICS (METALS AND WET CHEMISTRY)							
Aluminum	7429905	1 000	-	1 000 000 000	1 000	500	30
Antimony	7440360	4,300		49 000 000	300	50	7
Arsenic	7440382	4 600	--	2 000 000	100	50	3
Barium	7440393	75 000	--	1 000 000 000	1 000	50	2
Beryllium	7440417	51 000	--	1 000 000 000	500	50	2
Cadmium	7440439	1,200	--	230 000 000	200	50	1
Chromium (Total) [6]	7440473	3 300	--	140 000 000	2 000	50	3
Cobalt	7440484	800	--	48 000 000	500	50	1
Copper	7440508	32 000	--	1 000 000 000	1 000	50	3
Iron	7439896	6 000	--	1 000 000 000	5 000	500	70
Lead	7439921	21 000	--	100 000 000	1 000	50	1
Magnesium	7439954	8 000 000		6 700 000 000	4 000	5 000	20
Manganese	7439965	1 000	--	180 000 000	1 000	50	2
Mercury (total)	7439976	50	--	20 000 000	50	2 000	NA
Nickel	7440020	100 000	-	1 000 000 000	1 000	50	6
Selenium	7782492	400	--	130 000 000	200	50	10
Silver	7440224	100	-	200 000 000	100	50	4
Sodium	17341252	2,500 000	--	1 000 000 000	10 000	5 000	100
Thallium	7440280	2 300	-	15 000 000	500	50	1
Vanadium	7440622	72 000	-	1 000 000 000	1 000	50	20
Zinc	7440666	47 000		1 000 000 000	1 000	500	30
Cyanide	57125	200	--	250 000	100	400	NA
Ammonia-N (U.S. EPA 350.1)	7664-41 7	10 000 000	-	6 700 000 000	1 000	500	40
Nitrate-N (U S EPA 300 0)	14797 55 8	200 000	-	1 000 000 000	--	100	4
Nitrite-N (U S EPA 300 0)	14797-65-0	20 000		380 000 000	--	100	2
Total phosphorus as P (U S EPA 365 3)	7723140	1 300 000		1 000 000 000	--	100	NA

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
POLYCHLORINATED BIPHENYLS (PCBs)							
Total PCBs	1336363	240 000		7 900 000	330	20	NA[5]
Aroclor 1016	12674112	--	Part 201 N/A			10	NA[5]
Aroclor 1221	11104282		Part 201 N/A	--	--	20	NA[5]
Aroclor 1232	11141165	--	Part 201 N/A	--	--	10	NA[5]
Aroclor 1242	53469219		Part 201 N/A	--	--	10	NA[5]
Aroclor 1248	12672296	--	Part 201 N/A	--	--	10	NA[5]
Aroclor 1254	11097691	--	Part 201 N/A	--	--	10	NA[5]
Aroclor 1260	11096825	--	Part 201 N/A	--	--	10	NA[5]
VOLATILE ORGANIC COMPOUNDS							
1 1 1 Trichloroethane	71556	4 000	--	67 000 000 000	50	50 00	11 10
1 1,2,2 Tetrachloroethane	79345	170	--	68 000 000	50	50 00	13 80
1 1,2 Trichloroethane	79005	100	--	190 000 000	50	50 00	10 40
1 1 Dichloroethane	75343	15 000		33 000 000 000	50	50 00	9 06
1 1 Dichloroethylene	75354	62	--	62 000 000	50	50 00	19 80
1,2 4 Trichlorobenzene	120821	1 800	--	25 000 000 000	330	200 00	21 80
1,2 Dibromoethane (ethylene dibromide)	106934	20	--	18,000,000	20	200 00	0 73
1,2-Dichlorobenzene	95501	360	--	100 000 000 000	100	50 00	8 47
1,2 Dichloroethane	107062	100	--	150 000 000	50	50 00	11 40
1 2 Dichloropropane	78875	100		270 000 000	50	50 00	19 00
1 3 Dichlorobenzene	541731	170	--	170 000	100	50 00	10 20
1 4 Dichlorobenzene	106467	290		570 000 000	100	50 00	8 69
2 Butanone (MEK)	78933	44 000	--	67 000 000 000	750	2 000 00	322 00
2 Hexanone	591786	20 000	--	2 700 000 000	2 500	2 000 00	396 00
4-Methyl 2 pentanone (MIBK)	108101	36 000	--	140 000 000 000	2 500	2 000 00	340 00
Acetone	67641	15 000	--	390 000 000 000	1 000	2 000 00	240 00
Benzene	71432	100	--	470 000 000	50	50 00	10 50

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1,k]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[2] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[4] (µg/kg)	METHOD DETECTION LIMIT[4] (µg/kg)
Bromodichloromethane	75274	1 200	--	110 000 000	100	50 00	8 70
Bromoform	75252	1 600	--	3 600 000 000	100	50 00	27 90
Bromomethane	74839	200	--	330 000 000	200	50 00	21 70
Carbon disulfide	75150	16 000	--	47 000 000 000	250	50 00	15 90
Carbon tetrachloride	56235	100	--	170 000 000	50	50 00	13 00
Chlorobenzene	108907	940	--	4 700 000 000	50	50 00	9 33
Chloroethane	75003	8 600	--	670 000 000 000	250	50 00	17 30
Chloroform	67663	1 600	--	1 600 000 000	50	50 00	9 58
Chloromethane	74873	2 300	--	4 900 000 000	250	50 00	13 60
cis 1,2 Dichloroethylene	156592	1 400	--	2 300 000 000	50	50 00	11 60
cis 1 3 Dichloropropene	542756	170		780 000 000	100	50 00	8 90
Dibromochloromethane	124481	1 600	--	160 000 000	100	50 00	8 17
Dibromochloropropane	96128	10		13 000 000	10	200 00	99 10
Dichlorodifluoromethane	75718	95 000	--	3 300 000 000 000	250	50 00	16 60
Ethylbenzene	100414	360	--	13 000 000 000	50	50 00	9 74
Isopropyl benzene	98828	91 000	--	5 800 000 000	250	200 00	9 30
Methylene chloride	75092	100	--	8 300 000 000	100	200 00	19 30
Methyl-tert-butyl ether (MTBE)	1634044	800	--	200 000 000 000	250	50 00	15 00
Styrene	100425	2,200	--	6 900 000 000	50	50 00	9 43
Tetrachloroethylene	127184	100	--	6 800 000 000	50	50 00	14 00
Toluene	108883	2 800	--	27 000 000 000	100	50 00	9 75
trans 1 2 Dichloroethylene	156605	2 000		4 700 000 000	50	50 00	13 90
trans-1 3-Dichloropropene	542756	170	--	780 000 000	100	50 00	9 10
Trichloroethylene	79016	100	--	2 300 000 000	50	50 00	18 80
Trichlorofluoromethane	75694	52 000	--	3 800 000 000 000	100	50 00	17 00
Vinyl chloride	75014	40	--	890 000 000	40	50 00	21 10
m,p Xylenes	1330207	700	--	290 000 000 000	150	50 00	18 60

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[3] (µg/kg)
o Xylenes	1330207	700	--	290 000 000 000	150	50 00	7 85
SEMI VOLATILE ORGANIC COMPOUNDS							
2 4 5-Trichlorophenol	95954	39 000	--	23 000 000 000	330	330	20
2 4 6 Trichlorophenol	88062	330		1 300 000 000	330	330	13
2 4-Dichlorophenol	120832	380	--	5 100 000 000	330	330	20
2 4 Dimethylphenol	105679	7 400	--	4 700 000 000	330	330	63
2 4-Dinitrotoluene	121142	430		20 000 000	330	330	27
2 Chlorophenol	95578	440	--	19 000 000	330	330	20
2 Methylnaphthalene	91576	57 000	--	37 000 000	330	330	30
2 Methylphenols (J)	1319773	1 400	--	6 700 000 000	330	330	23
2 Nitrophenol	88755	400	--	2 900 000	330	330	20
3,3 Dichlorobenzidine	91941	2 000	--	8 200 000	2 000	330	100
4 6 Dinitro-2-methylphenol (2 methyl-4,6-dinitrophenol)	534521	830	--	360 000	830	330	20
4-Chloro 3-methylphenol	59507	280	--	20 000 000	280	330	20
4-Methylphenol (J)	1319773	1 400	--	6 700 000 000	330	330	23
Acenaphthene	83329	4 400	--	14 000 000 000	330	330	20
Acenaphthylene	208968	5 900	--	2 300 000 000	330	330	17
Anthracene	120127	41 000	--	67 000 000 000	330	330	17
Benzo(a)anthracene	56553	20 000	--	160 000	330	330	10
Benzo(a)pyrene	50328	2 000	--	1 900 000	330	330	13
Benzo(b)fluoranthene	205992	20 000	--	160 000	330	330	17
Benzo(g,h,i)perylene	191242	2 500 000	--	800 000 000	330	330	7
Benzo(k)fluoranthene	207089	200 000		1 600 000	330	330	20
bis(2 Chloroethyl)ether (I)	111444	100	--	12 000 000	100	330	37
bis(2 Ethylhexyl)phthalate	117817	2 800 000	--	890 000 000	330	330	30
Butyl benzyl phthalate	85687	26 000	--	47 000 000 000	330	330	23

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[2] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
Carbazole	86748	1 100	--	3 400 000	330	330	40
Chrysene	218019	2 000 000		16 000 000	330	330	13
Dibenzo(a,h)anthracene	53703	2 000		16 000	330	330	7
Dibenzofuran	132649	--	1 700	--	330	330	23
Diethyl phthalate	84662	2 200	--	3 300 000 000	330	330	17
Dimethyl phthalate	131113	790 000	--	3 300 000 000	330	330	17
Di-n-butylphthalate	84742	11 000	--	3 300 000 000	330	330	10
Di-n-octyl phthalate	117840	6 900 000	--	140 000 000	330	330	13
Fluoranthene	206440	5 500	--	9 300 000 000	330	330	27
Fluorene	86737	5,300	--	9,300 000 000	330	330	30
Hexachlorobenzene (C 66)	118741	350	--	8,500 000	330	330	23
Hexachlorobutadiene (C-46)	87683	91	--	180 000 000	50	330	40
Hexachlorocyclopentadiene (C 56)	77474	30,000	--	13 000,000	330	330	330
Hexachloroethane	67721	430	--	230 000 000	300	330	33
Indeno(1 2 3-cd)pyrene	193395	20 000	--	160 000	330	330	7
Isophorone	78591	11 000	--	12 000 000 000	330	330	17
Naphthalene	91203	870	--	200 000 000	330	330	27
Nitrobenzene (I)	98953	330	--	47 000 000	330	330	37
n Nitroso-di-n-propylamine	621647	330	--	2 000 000	330	330	23
N Nitrosodiphenylamine	86306	5 400		11 000 000	330	330	53
Pentachlorophenol	87865	22		130 000 000	20	330	30
Phenanthrene	85018	5,300	--	7,200 000	330	330	17
Phenol	108952	4,200	--	40 000 000 000	330	330	23
Pyrene	129000	480 000	--	6 700 000 000	330	330	40

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)	PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)

Notes

[1] The parameters included in this table are those included in the USEPA Contract Laboratory Program (CLP) Target Compound List (TCL) and Target Analyte List (TAL) except those that are not on the Part 201 list, Calcium, Potassium, 1,2,3 Trichlorobenzene Bromochloromethane Cyclohexane Methyl Acetate Methylcyclohexane (methyl phenol) 1 1 Biphenyl 2 2-oxybis(1 Chloropropane) 2 4-Dinitrophenol, 2,6 Dinitrotoluene 2 Nitroaniline 3 Nitroaniline 4-Bromophenyl phenylether 4-Chloroaniline 4-Chlorophenyl phenylether 4-Nitroaniline 4-Nitrophenol Benzaldehyde bis(2 Chloroethoxy)methane Or those that are not typically analyzed by WATS or CAS 1 1 2 Trichloro 1 2 2 triflouroethane 1 2 4 5 Tetrachlorobenzene Acetophenone Atrazine beta-Chloronaphthalene Caprolactum.

[2] The actual Quantitation Limits and Method Detection Limits will vary with sample size for the analysis of PCBs and PAHs

[3] Potentially applicable Michigan Part 201 Criteria are from the Michigan Department of Environmental Quality (MDEQ) Remediation and Redevelopment Division (RRD) Operational Memorandum No 1 dated January 23 2006

[4] VOC analysis will be conducted by Columbia Analytical Services. All other analyses will be conducted by Weyerhaeuser Analytical Testing Services

[5] The MDL actually achievable in a given analysis will vary depending on detector response characteristics irreducible noise from instrument electronics and matrix effects

[6] The Michigan Part 201 Criteria for Hexavalent Chromium will be used for Chromium (total) as there is no total chromium criteria established.

WATS = Weyerhaeuser Analytical Testing Service

NA = Not Available

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
METALS (TOTAL/SPLP) AND CYANIDE							
Aluminum	7429905	50	--	64 000 000	50	5	0 3
Antimony	7440360	6	--	68 000	2	0 5	0 07
Arsenic	7440382	10	--	4 300	5	0 5	0 03
Barium	7440393	2 000		14 000 000	100	0 5	0 02
Beryllium	7440417	4		290 000	1	0 5	0 02
Cadmium	7440439	5	--	190 000	1	0 5	0 01
Chromium (Total) [6]	7440473	11	--	460 000	10	0 5	0 03
Cobalt	7440484	40	--	2 400 000	20	0 5	0 008
Copper	7440508	1 000	--	7 400 000	4	0 5	0 03
Iron	7439896	300	--	58 000 000	200	0 5	0 7
Lead	7439921	--	4	--	3	0 5	0 006
Magnesium	7439954	400,000	--	1,000,000,000	1,000	50	0 2
Manganese	7439965	50	--	9 100 000	50	0 5	0 02
Mercury (total)[4]	7439976	0 0013	--	56	0 001	1 (ng/L)	0 06 (ng/L)
Methyl Mercury [4]	22967926	0 0013		56	0 001	0 1 (ng/L)	0 05 (ng/L)
Nickel	7440020	100 00	--	74 000 000	20	0 5	0 06
Selenium	7782492	5	--	970 000	5	0 5	0 1
Silver	7440224	0 2	--	1 500 000	0 2	0 5	0 04
Sodium	17341252	120 000	--	1 000 000 000	1 000	50	1
Thallium	7440280	2	--	13 000	2	0 5	0 007
Vanadium	7440622	5	--	970 000	4	0 5	0 2
Zinc	7440666	2 400	--	110 000 000	50	5	0 3
Cyanide	57125	5	--	57 000	5	9	3

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
POLYCHLORINATED BIPHENYLS (PCBs)							
Total PCBs	1336363	0 2	--	45	0 2	0 2	NA[5]
Aroclor-1016	12674112	--	Part 201 N/A			0 2	NA[5]
Aroclor 1221	11104282	--	Part 201 N/A	--	--	0 2	NA[5]
Aroclor 1232	11141165		Part 201 N/A		--	0.2	NA[5]
Aroclor 1242	53469219	--	Part 201 N/A			0 2	NA[5]
Aroclor 1248	12672296		Part 201 N/A			0 2	NA[5]
Aroclor 1254	11097691	--	Part 201 N/A	--		0 2	NA[5]
Aroclor 1260	11096825		Part 201 N/A		--	0.2	NA[5]
VOLATILE ORGANIC COMPOUNDS							
1 1 1 Trichloroethane	71556	200		1 300 000	1	0 5	0 13
1 1 2 2 Tetrachloroethane	79345	9		77 000	1	0 5	0 09
1 1,2 Trichloroethane	79005	5	--	110 000	1	0 5	0 10
1 1 Dichloroethane	75343	740	--	2 400 000	1	0 5	0 09
1 1-Dichloroethylene	75354	7		140 000	1	0 5	0 08
1 2 4 Trichlorobenzene	120821	30		300 000	5	0 5	0 07
1,2 Dibromoethane (ethylene dibromide)	106934	0 05	--	15,000	0 05	0 5	0 11
1,2 Dichlorobenzene	95501	16	--	160 000	1	0 5	0 06
1,2 Dichloroethane	107062	5	--	2 500 000	1	0 5	0 12
1,2 Dichloropropane	78875	5	--	2 800 000	1	0 5	0 09
1,3-Dichlorobenzene	541731	7	--	2 000	1	0 5	0 09
1 4-Dichlorobenzene	106467	13	--	74 000	1	0 5	0 11
2 Butanone (MEK)	78933	2,200	--	240 000 000	25	5	0 92
2 Hexanone	591786	1 000	--	8 700 000	50	5	0 84
4 Methyl 2 pentanone (MIBK)	108101	1 800		20 000 000	50	5	0 77
Acetone	67641	730	--	1 000 000 000	50	5	0 74
Benzene	71432	5		68 000	1	0 5	0 10

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[2] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
Bromodichloromethane	75274	80	--	37 000	1	0.5	0 08
Bromoform	75252	80	--	3 100 000	1	0 5	0 09
Bromomethane	74839	10	--	70 000	5	0 5	0 21
Carbon disulfide	75150	800	--	1 200 000	5	0 5	0 09
Carbon tetrachloride	56235	5	--	9 600	1	0 5	0 09
Chlorobenzene	108907	47	--	470 000	1	0 5	0 08
Chloroethane	75003	430	--	5 700 000	5	0 5	0 09
Chloroform	67663	80	--	180 000	1	0 5	0 07
Chloromethane	74873	260	--	490 000	5	0 5	0 15
cis 1,2 Dichloroethylene	156592	70		530 000	1	0 5	0 09
cis 1 3 Dichloropropene	542756	8 5	--	130 000	1	0 5	0 16
Dibromochloromethane	124481	80	--	110 000	5	0 5	0 09
Dibromochloropropane	96128	0 2	--	1 200	0 2	0 5	0 26
Dichlorodifluoromethane	75718	1 700	--	300 000	5	0 5	0 12
Ethylbenzene	100414	18	--	170 000	1	0 5	0 10
Isopropyl benzene	98828	800	--	56 000	5	0 5	0 15
Methylene chloride	75092	5	--	1 400 000	5	0 5	0 04
Methyl tert-butyl ether (MTBE)	1634044	40	--	47 000 000	5	0 5	0 12
Styrene	100425	80	--	310 000	1	0 5	0 07
Tetrachloroethylene	127184	5	--	200 000	1	0 5	0 12
Toluene	108883	140	--	530 000	1	0 5	0 09
trans-1,2 Dichloroethylene	156605	100		230 000	1	0 5	0 11
trans-1,3-Dichloropropene	542756	8 5	--	130 000	1	0 5	0 15
Trichloroethylene	79016	5	--	1 100 000	1	0 5	0 10
Trichlorofluoromethane	75694	2 600	--	1 100 000	1	0 5	0 08
Vinyl chloride	75014	2	--	33 000	1	0 5	0 06
m,p Xylene	1330207	35	--	190 000	3	0 5	0 27

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
o Xylene	1330207	35	--	190 000	3	0 5	0 12
SEMI VOLATILE ORGANIC COMPOUNDS							
2 4,5 Trichlorophenol	95954	730	--	170 000	5	10	0 6
2 4 6 Trichlorophenol	88062	4 4	--	10 000	4	10	0 4
2 4-Dichlorophenol	120832	19	--	48 000	10	10	0 6
2 4-Dimethylphenol	105679	370	--	520 000	5	10	1 9
2 4 Dinitrotoluene	121142	7 7	--	8 600	5	10	0 8
2-Chlorophenol	95578	22	--	94 000	10	10	0 6
2 Methylnaphthalene	91576	260		25 000	5	10	0 9
2 Methylphenol (J)	1319773	71	--	810 000	10	10	0 7
2 Nitrophenol	88755	20	--	79 000	5	10	0 6
3 3-Dichlorobenzidine	91941	0 3		180	0 3	10	3
4 6 Dinitro 2 methylphenol (2 methyl-4,6-dinitrophenol)	534521	20	--	9,500	20	10	0 6
4 Chloro-3 methylphenol	59507	7 4	--	79 000	5	10	0 6
4 Methylphenol (J)	1319773	71	--	810 000	10	10	0 7
Acenaphthene	83329	19	--	4,200	5	10	0 6
Acenaphthylene	208968	52	--	3 900	5	10	0 5
Anthracene	120127	--	43	--	5	10	0.5
Benzo(a)anthracene	56553	2 1	--	9 4	1	10	0 3
Benzo(a)pyrene	50328	1	--	5	1	10	0 4
Benzo(b)fluoranthene	205992	--	1 5	--	1	10	0 5
Benzo(g,h,i)perylene	191242	--	1	--	1	10	0 2
Benzo(k)fluoranthene	207089	--	1	--	1	10	0 6
bis(2-Chloroethyl)ether (I)	111444	1	--	17 000 000	1	10	1 1
bis(2 Ethylhexyl)phthalate	117817	6	--	340	5	10	0 9
Butyl benzyl phthalate	85687	14	--	2 700	5	10	0 7

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
Carbazole	86748	10	--	7 400	10	10	1 2
Chrysene	218019		1 6		1	10	0 4
Dibenzo(a,h)anthracene	53703		2		2	10	0 2
Dibenzofuran	132649		4		4	10	0 7
Diethyl phthalate	84662	110		1 100 000	5	10	0 5
Dimethyl phthalate	131113	73 000		4 200 000	5	10	0 5
Di n-butylphthalate	84742	9 7		11 000	5	10	0 3
Di n-octyl phthalate	117840	130		400	5	10	0 4
Fluoranthene	206440	1 6		210	1	10	0 8
Fluorene	86737	12		2 000	5	10	0 9
Hexachlorobenzene (C-66)	118741	0 2		3 000	0 2	10	0 7
Hexachlorobutadiene (C-46)	87683	0 05		3,200	0 05	10	1 2
Hexachlorocyclopentadiene (C-56)	77474	50		1 600	5	10	10
Hexachloroethane	67721	6 7		50 000	5	10	1
Indeno(1 2,3-cd)pyrene	193395		2		2	10	0 2
Isophorone	78591	570		12,000 000	5	10	0 5
Naphthalene	91203	13		31 000	5	10	0 8
Nitrobenzene (I)	98953	3 4		550 000	3	10	1 1
n Nitroso-di-n propylamine	621647	5		360	5	10	0 7
N Nitrosodiphenylamine	86306	270		35 000	5	10	1 6
Pentachlorophenol	87865	1		200	1	10	0 9
Phenanthrene	85018	2 4		1 000	2	10	0 5
Phenol	108952	210		29 000 000	5	10	0 7
Pyrene	129000		140		5	10	1.2

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)	PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)

Notes
(1) The parameters included in this table are those included in the USEPA Contract Laboratory Program (CLP) Target Compound List (TCL) and Target Analyte List (TAL) except those that are not on the Part 201 list Calcium, Potassium, 1 2,3 Trichlorobenzene Bromochloromethane Cyclohexane Methyl Acetate Methylcyclohexane (methyl phenol) 1 1 Biphenyl 2 2 oxybis(1 Chloropropane) 2,4-Dinitrophenol 2 6 Dinitrotoluene, 2 Nitroaniline 3 Nitroaniline 4-Bromophenyl phenylether 4-Chloroaniline 4 Chlorophenyl phenylether 4-Nitroaniline 4-Nitrophenol, Benzaldehyde bis(2 Chloroethoxy)methane Or those that are not typically analyzed by WATS or CAS 1 1 2 Trichloro 1 2 2 triflouroethane 1,2 4 5 Tetrachlorobenzene Acetophenone Atrazine beta-Chloronaphthalene Caprolactum.
(2) The actual Quantitation Limits and Method Detection Limits will vary with sample size, for the analysis of PCBs and PAHs
(3) Potentially applicable Michigan Part 201 Criteria are from the Michigan Department of Environmental Quality (MDEQ) Remediation and Redevelopment Division (RRD) Operational Memorandum No 1 dated December 10 2004
(4) Low level and methyl mercury will be analyzed by Columbia Analytical Services (CAS)
(5) The MDL actually achievable in a given analysis will vary depending on detector response characteristics irreducible noise from instrument electronics and matrix effects
(6) The Michigan Part 201 Criteria for Hexavalent Chromium will be used for Chromium (total) as there is no total chromium criteria established.
WATS = Weyerhaeuser Analytical Testing Service
NA = Not Available

QAPP Worksheet #15-4
Reference Limits and Evaluation (Free Product)

ANALYTE	CAS NUMBER	PROJECT ACTION LIMIT[1]	FREE PRODUCT (mg/kg)[2]	
			LABORATORY MDL	LABORATORY RL
PCBs (U S. EPA 8082)				
Aroclor 1016	12674-11 2	--	--	1 0
Aroclor 1221	11104-28 2	--	--	2 0
Aroclor 1232	11141 16-5	--	--	1 0
Aroclor 1242	53469 21 9	--	--	1 0
Aroclor 1248	12672 29-6		--	1 0
Aroclor 1254	11097-69 1			1 0
Aroclor 1260	11096-82 5		--	1 0
Total PCBs	1336-36-3		--	2 0
Physical Properties				
Specific Gravity (ASTM D854-83)	--	--	--	--

Notes

(1) Standards are consistent with the Multi Area Quality Assurance Project Plan (Rev 00) For the Kalamazoo River Study Group (Arcadis BBL 2007b) which are from the MDEQ s Substantive Requirements Document for the Plainwell Dam Superfund Site, dated February 13 2007 The TSS standards are on a monthly and daily basis, respectively

(2) Concentrations are in µg/L, except where noted.

(3) U.S EPA. *Appendix A to Part 136 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater Method 608—Organochlorine Pesticides and PCBs* July 1995

(4) U S EPA *Methods for Chemical Analysis of Water and Wastes* EPA/600/4-79/020 EMSL-Cincinnati 1983

(5) The actual Reporting Limit will depend on the volume of sample filtered.

RL = reporting limit.
MDL = Method Detection Limit
µg/L = micrograms per liter
mg/L = milligrams per liter
PCBs = polychlorinated biphenyls

QAPP Worksheet #16-5
Project Schedule/Timeline
Plainwell Mill Phase II RI Work Plan

ACTIVITIES	ORGANIZATION	DATES (MM/DD/YY)		DELIVERABLE	DELIVERABLE DUE DATE
		ANTICIPATED DATE(S) OF INITIATION	ANTICIPATED DATE OF COMPLETION		
Implementation of the Phase II RI	CRA	06/01/09	02/19/10	RI Report	80 Days After Completion of Field Activities and Notice to the U S EPA
Identification of Remedial Action Objectives	CRA	01/01/10	02/18/10	Screening Report	70 Days After U S EPA approval of the Draft
Feasibility Study	CRA	05/28/10	10/28/10	Feasibility Study Report	110 Days After U S EPA approval of the Draft

QAPP Worksheet #16-6
Project Schedule/Timeline
12th Street Landfill RA Work Plan

ACTIVITIES	ORGANIZATION	DATES (MM/DD/YY)		DELIVERABLE	DELIVERABLE DUE DATE
		ANTICIPATED DATE(S) OF INITIATION	ANTICIPATED DATE OF COMPLETION		
Completion of Remedial Design	CRA	08/19/09	07/20/09	Submittal 1[1] Submittal 2 and Final Submittal[2]	57 Days After Completion of Remedial Design Completion
RA Work Plan	CRA	November 2009	December 2009	RA Work Plan Report	39 Days After submitting Submittals to U S EPA
Preliminary RA Implementation Construction Work	CRA	04/05/10	10/06/10	Certification of Completion of Construction Report	In Accordance with RA Work Plan

(1) Submittal 1 was provided to U S EPA on May 27 2009

(2) Final Submittal will include all required elements at a final level of detail

QAPP Worksheet #17 5
Sampling Design and Rationale
Plainwell Mill Phase II RI Work Plan

Describe and provide a rationale for choosing the sampling approach (*e.g*, grid system, biased statistical approach)

Surface Water Quality

The surface water sample will be collected at a location near the southeast of the mill at millrace and one at a location near northeast of the mill at the Kalamazoo River as described in Worksheet #11 The samples will be analyzed to characterize the surface water quality and to determine the analytical needed for data comparison

Soil Sampling Activities

Soil samples will be collected at various locations/depths to further characterize the soil at the mill and to confirm the historical exceedances at some locations/depths

Groundwater Monitoring:

Site-wide groundwater monitoring will be performed at existing and new monitoring locations to further evaluate the groundwater beneath the site confirm the historical exceedances and to determine the next steps in investigation activities Vertical aquifer profiling will be conducted at two locations to collect formation water (i e groundwater) samples from different depths within the aquifer to determine the extent and distribution of potential contamination and to determine any residual groundwater impacts below the water table adjacent to the Kalamazoo River

Describe the sampling design and rationale in terms of what matrices will be sampled what analytical groups will be analyzed and at what concentration levels the sampling locations (including QC critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations)

Refer to Worksheet #18 5

QAPP Worksheet #17-6
Sampling Design and Rationale
12Th Street Landfill RA Work Plan

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach)

Asphalt Plant Property Soil Sampling

The collected soil samples will be submitted to laboratory for a quick turn analysis (24 to 72 hour) so the results can be reviewed and the adequacy of the excavation can be verified before restoring the excavated area.

MDNR Properties Soil Sampling:

The collected soil samples will be submitted to laboratory for a quick turn analysis (24 to 72 hour) so the results can be reviewed and the adequacy of the excavation can be verified before restoring the excavated area.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels the sampling locations (including QC critical, and background samples), the number of samples to be taken and the sampling frequency (including seasonal considerations)

Refer to Worksheet #18 5

QAAP Worksheet # 18-4
Area 1 Sampling Locations and Methods/SOP Requirements
Plainwell Mill Phase II RI Work Plan

ACTIVITY/ LOCATION	PROPOSED ASSESSMENT LOCATION			RATIONALE FOR LOCATION SELECTION	SAMPLE/ COLLECTION ETAILS	SAMPLE MATRIX	FIELD SCREENING	LABORATORY ARAMETERS	SAMPLE LOCATIONS	INVESTIGATIVE SAMPLES	QUALITY CONTRO SAMPLES			TOTAL BER OF SAMPLES
	DESIGNATION	TYPE	DEPTH (FT BGS)								TRIP LANKS	FIELD DUPLICATES	MS/MSDS	
Soil Sampling														
Lagoon through	SB-106 through SB-133	Soil Boring	20	Confirmation and determination of paper waste	- Collection of surface soil samples - Sampling Program	Soil	isual and Olfactory Evidence Impact and PID Screening	TCL VOCs TCL SVOCs Metals SPLP Metals PCBs General Chemistry	28	12		12		130
Lagoon J (SB-2)	MW 13	Monitoring Well ertical Aquifer Testing	20 (MW)	Determine the groundwater chemistry at the depth of the residual waste buried within the former lagoon area.										
SGWB-2	MW-14	Monitoring Well	20	T determine background groundwater chemistry south of the lagoons										
Former Secondary Clarifier	MW 15	Monitoring Well	20	T determine groundwater impacts associated with historical operations										
Former Secondary Clarifier	SB-138 SB-139 SB-140 SB-141	Soil Boring	20	determine extent of impact surrounding the former secondary clarifier						16				
Aeration Basin	SB-137	Soil Boring	20	determine extent of impact surrounding the aeration basin										
Areas adjacent the lagoons and Aeration Basin	SB-134 SB-135 SB-136	Soil Boring	20	define historical morphing the sizes of the lagoons and the aeration basin						12				13
North of Lagoon Area	SB-101 SB- 02 SB-103 SB- 04 SB-105	Soil Boring	20	T determine extent of potential paper waste north of the lagoon area adjacent the Kalamazoo River						20				25
Wooded Area	SB-142 SB-143 SB-144 SB- 45	Soil Boring	20	confirm no impacts associated with historical operations within this area. Location of samples will be dependent based on inspection of the area.	- Sample collection and location will be dependent on site walk through and field screening. - Collection one surficial soil sample -Sampling Program					12				14
Soil Physical Properties	SB-134 SB-135 SB-136 SB-137	Soil Boring/ Hand Auger		Collection of samples to determine the potential for vapor intrusion through native soil materials within the unsaturated zone	- Collection of one sample from hat is field screened as native material within the vadose zone			Soil Physical Properties			NA	NA		
								Soil Sampling Total	53	193				222
Groundwater Sampling														
MW-8, MW MW 10, MW 1, MW 12, MW 13, MW 14, MW-15		Groundwater Sample		T confirm on-Site groundwater quality	- Completion monitoring well inspection - Collection of groundwater levels and surface water levels (at associated staff gauges) - Collection of one groundwater sample per location	Groundwater	H, Conductivity emperature, Dissolved Oxygen, ORP Turbidity	TCL VOCs TCL SVOCs PCBs AL Inorganics						13
MW 13		ertical Aquifer Sampling Groundwater Samples	40	Complete vertical aquifer testing determine groundwater conditions below the confining unit	- Collection of groundwater samples every feet until the confining layer reached or 40 feet bgs			TCL OCs TCL SVOCs AL Metals (filtered)						
								Groundwater Sampling otal						

Notes:
Refer Page for able Notes

CRA 8/09

QAAP Worksheet # 18-4
Area 2 Sampling Locations and Methods/SOP Requirements
Plainwell Mill Phase II RI Work Plan

ACTIVITY / LOCATION	PROPOSED ASSESSMENT LOCATION			RATIONALE FOR LOCATION SELECTION	SAMPLE/DA COLLECTION DETAILS	SAMPLE MATRIX	FIELD SCREENING	LABORATORY ARAMETERS	SAMPLE LOCATIONS	INVESTIGATIVE SAMPLES	Q ALITY CONTROL SAMPLES			TOTAL NUMBER OF SAMPLES
	DESIGNATION	TYPE	DEPTH (FT BGS)								TRIP BLANKS	FIELD DUPLICATES	MS/MSD	
Soil Sampling														
TP- and TP-18	SB-201 SB-202 SB-203 SB-204	Soil Boring	20	Confirmation of noted potential contamination associated with the former Transformer Pad	- Collection of one surficial soil sample (SB-201 and SB-204 only) - Sampling Program	Soil	Visual and Olfactory Evidence of Impact and PID Screening	TCL VOCs TCL SVOCs AL Metals SPLP Metals PCBs General Chemistry						
Mill Building Outflow Points		Hand uger		Inspection and confirmation of capped outflows from the Mill Buildings	- Surface sampling only be conducted Impacts are suspected from field screening				4*					
Mill Building		Hand Auger		Inspection of soils around the perimeter of the Mill Buildings	- Surface sampling only be conducted Impacts are suspected from field screening				5*	5*				7*
North East of Mill Building	MW 16	Monitoring Well	20	Installation of monitoring well determine hydraulic connection with the Mill Race	- Sampling Program -Collection of one surficial soil sample									
South Parking Lot	MW 17	Monitoring Well	20	Installation of monitoring well determine hydraulic connection with the Mill Race	- Sampling Program									
Sou Parking Lot and BKS	TP-201 TP-202	est Pit	10	-Confirm the presence fill material beneath the parking lot area Determine potential impacts with historical activities	- Sampling Program - Collection of one surface sample (TP-202 only)									
Soil Physical Properties	SB-201 SB-202	Soil Boring/ Hand Auger		Collection of samples determine the potential for vapour intrusion through native soil materials within the unsaturated zone	- Collection of one sample from what field screened as native material within the unsaturated, vadose zone			Soil Physical Properties			NA			
								Soil Sampling Total		36				42
Groundwater Sampling														
MW 1, MW-2, MW-3, MW-4, MW-5, MW 16 MW		Groundwater Sample		T Confirmation of on-Site groundwater chemistry	- Completion of monitoring well inspection - Collection of groundwater and surface water levels (associated staff gauges) - Collection of one groundwater sample per location	Groundwater	pH, Conductivity emperature, Dissolved Oxygen, ORP urbidity	TCL VOCs TCL SVOCs PCBs AL Inorganics						12
MW	A-2	ertical Aquifer esting-Groundwater Samples	40	Complete vertical aquifer testing to determine groundwater conditions below the confining unit	- Collection of groundwater samples every feet until the confining layer is reached or 40 feet bgs			TCL VOCs TCL SVOCs Metals (filtered)						11
								Groundwater Sampling otal		15				23
Surface Water Sampling														
Mill Race and Kalamazoo River	SW-001 SW-002	Surface Water Sample		Confirm surface water quality of the Mill Race and Kalamazoo River related to mercury Determine analytical data needed for data comparison.	- Collection of two surface water samples -Collection of surface water levels	Water	pH, Conductivity emperature, Dissolved Oxygen, ORP urbidity	Low level Mercury Methyl Mercury Hardness						
								Surface Water Sampling Total						

Notes:
Refer Page for able Notes

QAAP Worksheet # 18-4
Area 3 Sampling Locations and Methods/SOP Requirments
Plainwell Mill Phase II RI Work Plan

ACTIVITY/ LOCATION	PROPOSED ASSESSMENT LOCATION			RATIONALE FOR LOCATION SELECTION	SAMPLE/DA COLLECTION DETAILS	SAMPLE MATRIX	FIELD SCREENING	LABORATORY ARAMETERS	SAMPLE LOCATIONS	INVESTIGATIVE SAMPLES	QUALITY CONTROL SAMPLES			TOTAL NUMBER OF SAMPLES
	DESIGNATION	TYPE	DEPTH (FT BGS)								TRIP BLANKS	FIELD UPLICATES	MS/MSD MS/DUP	
Soil Sampling														
DG3 and DG4 (Area 3)	SB-301, SB-302	Soil Boring	20	Confirmation of impact noted in historical sampling	- Collection of one surface soil sample - Sampling Program	Soil	Visual and Olfactory Evidence of Impact and PID Screening	TCL VOCs, TCL SVOCs AL Metals SPLP Metals PCBs General Chemistry	2					
SGWB-10	MW 18	Monitoring Well	20											
SGWB-3	SB-321	Soil Boring	20											
Coal Pile Storage Area (Area 3C)	TP-308 TP-309 TP-310 TP-31 TP 12 TP-313 TP-3 TP-315	est Pi		Confirmation of extent of coal impacts	Collection of up to surface soil samples - Sampling Program					21				24
No. Fuel Oil Tank Area (Area 3D)	SB-303 SB-304 SB-305 SB-306 SB-307	Soil Boring	10	Confirmation of impacted soil removal activities	- Sampling Program					20				20
SGW (Area 3D)	MW	Monitoring Well	20	Confirmation of historical groundwater impacts	- Collection of one surficial soil sample-Sampling Program 2									
Former Coal Tunnel (Area E)	SB-308 SB-309 SB-31 SB-311 SB-312	Soil Boring		Confirmation f potential contamination noted in historical sampling	Collection of up 3 surface samples Sampling Program					13				
Undeveloped Lands	TP-301 TP-302 TP-303 TP-304 TP-305 TP-306 TP-307	Test Pi	10	-Confirm the presence of fill material beneath the parking lot area -Determine potential impacts ith historical activities	Collection of surficial soil samples Sampling Program					21				24
Soil Physical Properties (Undeveloped Lands)		Soil Boring/ Hand ugar	5	Collection of samples to determine the potential for vapour intrusion through native soil materials within the unsaturated zone	- Collection of one sample from what field screened as native material ithin the vadose zone			Soil Physical Properties				NA	NA	
								Soil Sampling Total	30	95				05
Groundwater Sampling														
MW-6, MW MW 8, MW		Groundwater Sample		Confirmation of on-Site groundwater chemistry	Completion of monitoring well inspection - Collection of groundwater and surface water levels (at associated staff gauges) Collection of one groundwater sample per location	Water	pH, Conductivity emperature, Dissolved Oxygen, ORP Turbidity	TCL OCs TCL SVOCs PCBs AL Inorganics						
								Groundwater Sampling Total						

Notes:
Refer to Page for able Notes

QAAP W rksheet # 18-4
Notes
Plainwell Mill Phase II RI Work Plan

Notes:

(1) Soil samples for analysis of SPLP will be collected and placed on hold pending results of TAL metal analysis

(2) General Chemistry Nitrogen compounds and phosphorous

(3) Soil Physical Properties- grain size analysis, dry bulk density porosity moisture content, fraction of organic carbon

( ) TAL Inorganics- TAL Metals plus low level mercury methly mercury and cyanide

(5) Sampling Program 1 One biased sample will be collected from the fill material from depth of 2 to 10 feet bgs based on field screening. If no impact ted, on soil sampl will be collected from 0 to 2 feet abov the interf ce between the fill/ native material within the
One soil sample from 0 to 2 feet below the bserved impacts If no impact observed the soil sample will be collected from 0 to 2 feet below the interface of the fill/ nati material within the vadose zone.
One soil sample will be collected from the adose zone, 0 to 2 feet above the saturated zone

( ) Sampling Program 2 If no mpact noted, discrete soil sample will be collected from 0 to 2 feet below th interface of the vadose and saturated zone. If impact noted one soil sampl will be collected within 2 to 10 feet bgs and third sampl collected from 0 to 2 feet.

(7) Sampling Program 3 One surficial soil sample will be collected from the 0 to 1 foot bgs. In case of presence of non-soil materials (e.g., gravel fill or concrete slab) the soil sample will be collected from 0 to 1 foot below the non-soil materials.
One biased soil sample will be collected from the fill material which is expected to encounter t approximately depths of 2 to 10 feet bgs based field screening methods including elevated PID readings and visual and olfactory evidence of impact and with special attention to lithological changes. Soil borings not exhibiting any evidence of impact will be sampled at 0 to 2 feet above the interface of fill/native material w thin dose zone
One soil sample will be collected from 0 to 2 feet below the bserved contamination. If evidence of impact is bserved the soil sample will be collected from 0 to 2 feet below the interface of fill/native material within adose zone
One soil sample will be collected from adose zone t 0 to 2 feet above the saturated zone

Sampling to be conducted if necessary the noted number of locations are subject to change depending on field findings
bgs below ground surface
MS/MSDs Matrix Spike/Matrix Spike Duplicates
SPLP Synthetic Precipitation Leaching Procedure
TAL Target Analyte List
TCL Target Compound List
VAS- Vertical Aquifer Sampling
VOC Volatile Organic Compound
SVOC Semi Volatil Organic Compound
PCB Polychlorinated Biphenyls
ORP Oxidati Reduction Potential
PID Photoionization Detector
NA Not Applicabl

Surficial Soil sample will be collected from 0 to 1 foot bgs. If non-soil materials are present (i.e gravel fill or concrete slab) the soil sample will be collected from 0 to 1 foot below the non-soil material
Field Screening will consist of PID readings to determine the presence of undifferentiated volatile organi vapors, visual screening for lithologic changes, stained soils residuals, and olfactory evidence of impacts.
Collect soil samples on continuous basis t 2 feet intervals
Collection of all samples as per Field Sampling Plan and Quality Assurance Project Plan including the references listed below
Samples to be submitted on regular turn around time.
All necessary MS/MSDS and Field Duplicates will be added where required
Groundwater samples will be collected using low flow techniques with the exception of VAS sampling which will be field filtered for metals analysis
Test pit length is 5 to 10 feet

Field Sampling References:

Sample Type	*Reference Document*	*Procedure*
Soil Sampling with Direct Push Sampler	FSP	Standard Operating Procedure F-5
Surficial Soil Sampling	FSP	Standard Operating Procedure F-6
Excavation and Test P ts and Test Pit Soil Sampling	FSP	Standard Operating Procedure F-8
Photoionization Detector (PID) Screening	FSP	Standard Operating Procedure F-9
Monitoring Well Installation	FSP	Standard Operating Procedure F-15
Groundw ter Sampling	FSP	Standard Operating Procedure F-11
Surface W ter Sampling	FSP	Standard Operating Procedure F-16
Staff Gauge Installation and Measurement	FSP	Standard Operating Procedure F-10
Vertical Aquifer Sampling	FSP	Standard Operating Procedure F-17
Sample Handling and Analysis/ Quality Assurance	FSP/ QAPP	Section 4/ Section 4.4.4 (with reference to QAPP Worksheets)
Sampl Labeling	FSP	Section 3 1
Chain-of-Custody Records	FSP	Section 3.3
Management of Investigation-derived Waste	FSP	Section 6.0
F eld Physical Measurements/ Surveying	FSP	Section 5 0/ Section 5 1
Hand Augering	FSP	Standard Operating Procedure F-6

QAPP Worksheet #18-5
Sampling Locations and Methods/SOP Requirements
12th Street Landfill RA Work Plan

SAMPLING LOCATION/ID NUMBER	MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	NUMBER OF SAMPLES[2] (identify field duplicates)	SAMPLING SOP REFERENCE[1]	RATIONALE FOR SAMPLING LOCATIONS
Asphalt Plant Property	Soil	Total PCBs	Not applicable	Nine samples one filed duplicates and one MS/MSDS sample will be collected, the exact number of samples and QA/QC samples to be collected will be determine following completion of excavation activities	F 6	The results of the sampling activities will verify the adequacy of the excavation limits before restoring the excavation area.
		TCL VOCs	Not applicable		F-6	The results of the sampling activities will verify the adequacy of the excavation limits before restoring the excavation area
MDNR Properties	Soil	Total PCBs	Not applicable	13 samples one filed duplicates and one MS/MSDS sample will be collected, the exact number of samples and QA/QC samples to be collected will be determine following completion of excavation activities	F-6	Surface samples (*i e* 0 to 6 inches) obtained to verify removal effectiveness

Footnotes

(1) See Project Sampling SOP References table (Worksheet #21)

(2) Field duplicates will be collected at a frequency of one duplicate for every 10 samples (Worksheet #20)

QAPP Worksheet #19
Analytical SOP Requirements

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION METHOD/SOP REFERENCE[1]	SAMPLE VOLUME	CONTAINERS (number size, and type)	PRESERVATION REQUIREMENTS (chemical, temperature, light protected)	MAXIMUM HOLDING TIME (preparation/ analysis)
Water	PCBs	All	W 1 (AM E-608)	2 liters	Two 1 liter amber glass bottles with Teflon® lined lid	Cool to 4 C ±2	14 days to extraction, 40 days to analysis
Water	TSS	All	W 2 W 5 (AM E 160 2) (AQ O DLYCHK)	1 liter	One 1 liter plastic container	Cool to 4 C ±2	7 days to analysis
Water	Total phosphorus	All	W 3 (AM E 365 3)	500 mL	One 500 mL plastic container	H_2SO_4 to pH<2 cool to 4 C	28 days to analysis
Water	TAL metals (total)	All	W 14 (AM E 200 8M)	500 mL	1 x 1 000-mL high density polyethylene bottle	Cool to 4 C add nitric acid to pH <2	6 months
Water	Total cyanide and amenable cyanide	All	W 25 (AM E 335 2 CLP M)	500 ml	1 x 500 ml plastic bottle	Sodium Hydroxide to pH ≤ 12 Cool to 4 C	14 days
Water	Low level mercury (total)	All	C-4 (MET 1631)	500 mL	1 x 500 mL fluorinated LPE bottle	Add HCl to pH <2 2 5 mL of BrCl is added at laboratory	48 hrs unpreserved, 90 days preserved to analysis
Water	Methyl Mercury	All	C 7 (MET 1630W)	500 mL	1 x 500 mL fluorinated plastic bottle	Dark, Cool to 4°C add HCl to pH <2 in clean polyethylene bag	180 days to analysis
Water	SVOCs	All	W 15 (AM E 8270)	1 000 mL	2 x 1 000 mL amber glass bottle Teflon® lined cap	Cool to 4 C protect from light	Extract within 7 days analyze within 40 days of extraction
Water	VOCs	All	W 21 (AM E 8260)	1 x 40 mL VOA vial	3 x 40 mL glass VOA vials with Teflon® septum	Cool to 4 C add HCl to pH <2 protect from light	14 days (sample should remain on site less than 24 hours)

QAPP Worksheet #19
Analytical SOP Requirements

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION METHOD/SOP REFERENCE[1]	SAMPLE VOLUME	CONTAINERS (number size and type)	PRESERVATION REQUIREMENTS (chemical, temperature, light protected)	MAXIMUM HOLDING TIME (preparation/ analysis)
Water	Hardness	All	W 26 (AM S 2340B)	500 mL	1 x 1 000 mL high density polyethylene bottle	Cool to 4 C add nitric acid to pH <2	6 months
Soil/Sediment	PCBs	All	W-4 (AM E-8082)	200 grams	One 8-oz glass jar with Teflon® lined lid	Cool to 4 C ±2	14 days to extraction, 40 days to analysis
Soil	Metals	All	W 14 (AM E 200 8M)	50 grams	One 500-mL amber glass bottle with Teflon® lined lid	Cool to 4 C ±2	6 months
Soil	Cyanide	All	W 25 (AM E 335 2 CLP M)	10 grams (at least)	One 8 oz wide mouth glass jar	Cool to 4 C ±2	14 days
Soil	SVOCs	All	W 15 (AM E 8270)	100 grams	One 500 mL amber glass bottle with Teflon® lined lid	Cool to 4 C ±2	14 days
Soil	VOCs	All	C 5 C-6 (VOC 8260 VOC 5035)	5 grams	1x40-mL VOA vials	Vial containing 5 ml Methanol cool to 4 C ±2	14 days
Soil	GRO DRO	All	W 22, W 23 (AM U WTPH D AM U WTPH G)	100 grams	WTPH D One 500 mL amber glass bottle with Teflon® lined lid WTPH G-4 oz jar with Teflon® lined lid	Cool to 4 C ±2	14 days
Soil	Ammonia N	All	C 9 (GEN 350 1)	100 grams	One 500 mL amber glass bottle with Teflon® lined lid	Cool to 4 C ±2	7 days to extraction 28 days to analysis (preserved with 9N sulfuric acid)
Soil	Nitrate-N	All	C 8 (GEN 353 2)	50 grams	One 8 oz wide mouth glass jar	Cool to 4 C ±2	7 days to extraction 28 days to analysis

QAPP Worksheet #19
Analytical SOP Requirements

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION METHOD/SOP REFERENCE[1]	SAMPLE VOLUME	CONTAINERS (number size, and type)	PRESERVATION REQUIREMENTS (chemical, temperature, light protected)	MAXIMUM HOLDING TIME (preparation/ analysis)
Soil	Nitrite-N	All	C 8 (GEN 353 2)	50 grams	One 8 oz wide mouth glass jar	Cool to 4 C ±2	7 days to extraction 48 hours to analysis
Soil	Phosphorous Total	All	C 10 (GEN 365 3)	50 grams	One 8 oz wide mouth glass jar	Cool to 4 C ±2	28 days
Free product	PCBs	All	C 13 C 14 (SOC 8082Ar) (EXT 3580)	3L	3 x 1L Glass	None	14 days to extraction, 40 days to analysis
Free Product	Specific Gravity	Not Applicable	C 16 (GEN-SPECGRAV)	500 mL	500 mL Plastic	None	None

Footnote

(1) See the Analytical SOP Reference (Worksheet #23)

QAPP Worksheet #20
Field Quality Control Sample Summary

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION SOP REFERENCE[1]	NUMBER OF SAMPLING LOCATIONS	NUMBER OF FIELD DUPLICATE PAIRS	MATRIX SPIKES	NUMBER OF TRIP BLANKS	NUMBER OF EQUIPMENT BLANKS	TOTAL NUMBER OF SAMPLES TO LABORATORY
Water	PCB	All	W 1	TBD	1/10	1/20	NA	1/10	TBD
Water	TSS	All	W 2 W 5	TBD	1/10	NA	NA	1/10	TBD
Water	Total phosphorus	All	W 3	TBD	1/10	1/20	NA	1/10	TBD
Water	TAL metals (total)	All	W 14	TBD	1/10	1/20	NA	1/10	TBD
Water	Total cyanide and amenable cyanide	All	W 24	TBD	1/10	1/20	NA	1/10	TBD
Water	Hardness	All	W 26	TBD	1/10	1/20	NA	1/10	TBD
Water	Low level mercury (total)	All	C-4	TBD	1/10	1/20	TBD	1/10	TBD
Water	Methyl Mercury	All	C 7	TBD	1/10	1/20	NA	1/10	TBD
Water	SVOCs	All	W 15	TBD	1/10	1/20	NA	1/10	TBD
Water	VOCs	All	W 21	TBD	1/10	1/20	TBD	1/10	TBD
Soil/Sediment	PCB	All	W-4	TBD	1/10	1/20	NA	1/10	TBD
Soil	Metals (total/SPLP)	All	W 14 W 25	TBD	1/10	1/20	NA	1/10	TBD
Soil	Ammonia N	All	C 9	TBD	1/10	1/20	NA	1/10	TBD
Soil	Nitrate N	All	C 8	TBD	1/10	1/20	NA	1/10	TBD
Soil	Nitrite N	All	C 8	TBD	1/10	1/20	NA	1/10	TBD
Soil	Phosphorous	All	C 10	TBD	1/10	1/20	NA	1/10	TBD
Soil	SVOCs	All	W 15	TBD	1/10	1/20	NA	1/10	TBD
Soil	VOCs	All	W 21	TBD	1/10	1/20	TBD	1/10	TBD
Soil	GRO DRO	All	W 22 W 23	TBD	1/10	NA	TBD	1/10	TBD
Free product	PCBs	All	C 13	TBD	1/10	1/20	NA	1/10	TBD

QAPP Worksheet #20
Field Quality Control Sample Summary

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION SOP REFERENCE[1]	NUMBER OF SAMPLING LOCATIONS	NUMBER OF FIELD DUPLICATE PAIRS	MATRIX SPIKES	NUMBER OF TRIP BLANKS	NUMBER OF EQUIPMENT BLANKS	TOTAL NUMBER OF SAMPLES TO LABORATORY
Free Product	Specific Gravity	Not Applicable	C 16	TBD	NA	NA	NA	NA	NA

Footnote
(1) See Analytical SOP Reference (Worksheet #23)

Note
NA = not applicable
TBD = to be determined

QAPP Worksheet #21
Project Sampling SOP Reference

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	ORIGINATING ORGANIZATION	EQUIPMENT TYPE	MODIFIED FOR PROJECT WORK? (Y/N)	COMMENTS
F 1	Water Sampling and Field Measurement Procedures	RMT	Kemmerer water sampler peristaltic pump automated sampler appropriate sample containers	Y	Sample method is dependent on water conditions at the sample location and specified analysis required
F 2	Surface Water Flow Measurement Procedures	RMT	electromagnetic velocity meter	Y	--
F 3	Water Treatment System Monitoring Procedures	RMT	appropriate sample containers	Y	--
F-4	Sediment Sampling Procedures	RMT	Trowel, stainless steel scoop bucket auger tube auger coring device	Y	Sample method is dependent of sediment site characteristics
F 5	Soil Sampling Procedures Direct Push Sampler	RMT		Y	--
F-6	Surficial Soil Sampling Procedures	RMT	Trowel stainless steel scoop	--	Confirmation sampling will consist of collecting surficial soil samples
F 7	Soil Gas Monitoring	RMT	Geoprobe® rods utilizing the Post Run Tubing (PRT) system and drive point or its equivalent, tubing Landtec gas monitor or its equivalent	Y	--

QAPP Worksheet #21
Project Sampling SOP Reference

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	ORIGINATING ORGANIZATION	EQUIPMENT TYPE	MODIFIED FOR PROJECT WORK? (Y/N)	COMMENTS
F 8	Excavation of Test Pits and Test Pit Soil Sampling	RMT	Stainless steel shovels trowels spoons or spatulas Backhoe Equipment	Y	--
F 9	Photoionization Detector (PID) Screening	RMT	--	Y	--
F 10	Staff Gage Installation and Measurement Procedure	RMT	Stadia rod, circular bubble level, laser level instrument	Y	
F 11	Groundwater Sampling Procedures	CRA	Bladder pump peristaltic pump or its equivalent	Y	--
F 12	Ambient Air Monitoring for Fugitive Dust	RMT	High volume air pump	Y	--
F 13	Ambient Air Monitoring for VOCs	RMT	High volume air pump	Y	
F 14	Real Time Turbidity Measurement Procedures for Surface Water	RMT	--	Y	
F 15	Monitoring Well Installation Procedures	RMT	--	Y	--
F 16	Surface Water Sampling Procedure	CRA	Dip sampler Kemmerer or Van Dorn bottles Line and messengers and Peristaltic pumps	Y	--
F 17	Vertical Aquifer Sampling	CRA	Bailer	Y	--

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection

FIELD EQUIPMENT	CALIBRATION ACTIVITY	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
Multi parameter Water Quality Meter	F 1	Per SOP and manufacturer s specifications	Turbidity temperature pH, conductivity DO	Check membranes and verify accurate operation	Daily	F 1	F 1	F 1	F 1 and Manufacture s Operations Manual
ISCO sampler or equivalent	Verify sample volumes	Battery charging	Collecting appropriate sample volumes	Check battery operation and tubing	Daily	F 1	F 1	F 1	F 1
Landtec gas sampler or equivalent	F 7	Per manufacturer s specifications	Measuring concentration of methane carbon dioxide and oxygen	Check tubing and sample port integrity	Daily	F 7	F 7	F 7	F 7
Magnehelic pressure gauge or equivalent	F 7	Per manufacturer s specifications	Measuring pressures	Check tubing and sample port integrity	Daily	F 7	F 7	F 7	F 7
Photoionization Detector	F 9	Per manufacturer s specifications	Measuring photoionizati on in soil	Check sample device	Daily	F 9	F 9	F 9	F 9
Flow Through Cell	F 11	Per manufacturer s specifications	temperature turbidity dissolved oxygen, specific electrical conductance and pH electrodes	Check sample device	Daily	F 11	F 11	F 11	F 11

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection

FIELD EQUIPMENT	CALIBRATION ACTIVITY	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
Peristaltic Pump or equivalent	F 11	Per manufacturer s specifications		Check sample device	Daily	F 11	F 11	F 11	F 11
Water Level Meter	F 11	Per manufacturer s specifications	Water levels	Check sample device	Daily	F 11	F 11	F 11	F 11

[1] See Project Sampling SOP Reference table (Worksheet #21)

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
W 1	Organochlorine and PCB (aroclor) pesticide analysis by GC/ECD AM E 608 September 11 2007	Definitive	Total PCB in water	Gas chromatography/ Electron capture detectors (GC/ECD)	Weyerhaeuser Analysis and Testing Services (WATS)	N	No – Approved by EPA with last version of Multi Area QAPP
W 2	Suspended solids in water and wastewater AM E 160 2 July 13 2007	Definitive	TSS	Balance	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W 3	Total and total soluble phosphorus in water AM E 365 3 August 19 2008	Definitive	Total phosphorus as P in water	Spectrophotometer	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W-4	Polychlorinated biphenyl analysis by GC/ECD AM E 8082 December 4 2007	Definitive	Total PCB in soil and sediment	GC/ECD	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W 5	Daily balance water and temperature checks AQ-O-DLYCHK, February 21 2007	Definitive	TSS	Balance	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W 6	General Procedures for Performing Chromatographic Separations and Calibrations AL G 8000 September 11 2007	Definitive	General Procedures	Not Applicable	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W 7	Sample Management Procedures OP S SMO July 13 2007	Definitive	Sample Management	Not Applicable	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W 8	Procedure for Training Personnel to Perform Test Methods and Standard Operating Procedures OQ TRAIN August 19 2008	Not applicable	Training	Not Applicable	WATS	N	No – Approved by EPA with last version of Multi Area QAPP
W 9	Analytical Procedure 3500 AC G 3500 August 15 2008	Definitive	PCBs and SVOCs in water	Not Applicable	WATS	N	Yes – But revised by WATS 7/07 per comment 10 6 in 6/07 EPA Letter

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
W 10	Extraction by Continuous Liquid Liquid Extractor AC G 3520 August 19 2008	Definitive	VOCs SVOCs and PCBs in water(1)	Not Applicable	WATS	N	Yes – See Footnote (1) per Comment 10 8 in 6/07 EPA Letter
W 11	Sonication for Soil and Sediments AC G 3550 July 13 2007	Definitive	PCBs and SVOCs in soil and sediment(2)	Not Applicable	WATS	N	Yes – See Footnote (2) per comment 10 7 in 6/07 EPA Letter
W 12	Acid Digestion of Aqueous Samples & Extracts for Metals Analysis by ICP & ICPMS AM E 3010 March 6 2007	Definitive	Metals in water	Not Applicable	WATS	N	No – Comment 12 in 6/07 EPA letter was suggestion only
W 13	Acid Digestion of Sediments Soils Sludges, and Other Solid Samples for Analysis by ICP & ICPMS AM E 3050 March 6 2007	Definitive	Metals in soil	Not Applicable	WATS	N	No Comment 13 in 6/07 EPA letter was suggestion only
W 14	Metals Analysis by ICPMS AM E 200 8M August 15 2008	Definitive	Metals in water and soil	Inductively Coupled Plasma Mass Spectrometer (ICPMS)	WATS	N	Yes – Replaced per Comment 16 in 6/07 EPA Letter
W 15	Capillary GC/MS for Semivolatile Organics AM E-8270 July 20 2007	Definitive	SVOCs in water and soil	GC/MS capillary column	WATS	N	Yes – But revised by WATS 6/07 per comment 10 10 in 6/07 EPA Letter Revised by WATS 6/09
W 16	Total Solids in Solid and Semi Solid Samples AM S 2540G August 19 2008	Definitive	Total solids in soil and sediment	Scale	WATS	N	Added per U S EPA 6/07 Comments
W 17	Procedure for Florisil Clean Up of Organic Extracts AC G 3620 September 11 2007	Definitive	PCBs in water soil and sediment	Not applicable	WATS	N	Added per U S EPA 6/07 Comments

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
W 18	Gel Permeation Clean Up AP E 3640 August 19 2008	Definitive	PCBs and SVOCs in water soil, and sediment	Not applicable	WATS	N	Added per U S EPA 6/07 Comments
W 19	Condensation and Evaporation Techniques AC G-CONC August 19 2008	Definitive	PCBs and SVOCs in water soil, and sediment	Not applicable	WATS	N	Added per U S EPA 6/07 Comments
W 20	Organic Laboratory Analytical Standards AC G ORGSTD July 18 2007	Definitive	VOCs SVOCs and PCBs in water soil, and sediment	Not applicable	WATS	N	Added per U S EPA 6/07 Comments
W 21	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry AM E 8260 August 27 2008	Definitive	VOCs in water	GC/MS	WATS	N	
W 22	Diesel and Motor Oil Range Compounds Analysis of AM U WTPH D August 20 2008	Definitive	Diesel range compounds	GC/FID Capillary column	WATS	N	
W 23	Gasoline Range Compounds Analysis of AM U WTPH G August 19 2008	Definitive	Gasoline range compounds	GC/FID megabore column	WATS	N	
W 24	Cyanide Total, AM E 335 2 CLP M August 27 2008	Definitive	Cyanide	Spectrophotometer	WATS	N	
W 25	Synthetic Precipitation Leaching Procedure (SPLP) AM E 1312 March 31 2003	Definitive	Metals in soil	Not applicable	WATS	N	
26	Hardness by Calculation, AM S 2340B June 12, 2007	Definitive	Hardness in water	Not applicable	WATS	N	
C 1	Sample Disposal, SMO-SDIS Rev 7 March 26 2008	Not Applicable	Sample Disposal	Not Applicable	Columbia Analytical Services (CAS)	N	

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
C 2	Sample Tracking and Internal Chain of Custody SMO SCOC Rev 12 April 23 2009	Not Applicable	Chain of Custody	Not Applicable	CAS	N	
C 3	Sample Receiving SMO-GEN Rev 25 April 9 2009	Not Applicable	Sample Receiving	Not Applicable	CAS	N	--
C-4	Mercury in Water by Atomic Fluorescence Spectrometry MET 1631 Rev 9 March 21 2008	Definitive	Low flow mercury in water	Cold Vapor Atomic Fluorescence Spectrometer (CVAFS)	CAS	N	
C 5	Volatile Organic Compounds by GC/MS VOC 8260 REV 12 March 21 2008	Definitive	VOCs in soil or water	GC/MS Capillary column	CAS	N	--
C-6	Purge and Trap/extraction for volatile organics in soil and waste samples, closed system. VOC 5035 REV 7 February 1 2008	Definitive	VOCs in soil and waste	Not applicable	CAS	N	--
C 7	Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap and CVAFS Rev 0 MET 1630W April 12 2006	Definitive	Low Level Mercury in Water	Cold Vapor Atomic Fluorescence Spectrometer (CVAFS)	CAS	N	
C-8	Nitrate/Nitrite Nitrite By Flow Injection Analysis GEN 353 2, Rev 6 January 5 2006	Definitive	Nitrate/Nitrite in Soil	Flow injection Analyzer	CAS	N	--
C 9	Ammonia By Flow Injection Analysis GEN 350 1 Rev 7 May 1 2007	Definitive	Ammonia N in Soil	Flow injection Analyzer	CAS	N	--
C 10	Phosphorous Determination Using Colorimetric Procedure GEN 365 3 Rev 10 August 28 2008	Definitive	Phosphorus in Soil	Spectrophotometer	CAS	N	

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
C 11	Laboratory Balance Monitoring and Calibration, (ADM BAL 1) August 7 2008	Definitive	Various (Weighing samples standards and reagents)	Balance	CAS	N	
C 12	Corrective Action (ADM CA) Rev 5 September 12 2007	Not Applicable	Corrective Action	Not Applicable	CAS	N	--
C 13	PCBs as Aroclors (SOC 8082AR) Rev 13 June 25 2009	Definitive	PCBs in oil	GC/ECD	CAS	N	
C 14	Waste Dilution Extraction (EXT 3580) Rev 2 April 30 2007	Definitive	PCBs in oil	Not Applicable	CAS	N	
C 15	Sulfuric Acid Cleanup (EXT 3665) Rev 2 April 30 2007	Definitive	PCBs in oil	Not Applicable	CAS	N	--
C 16	Specific Gravity (Gen SPGRAV) Rev 0 June 6 2006	Definitive	Specific Gravity	Hydrometer	CAS	N	

Notes
(1) See appropriate analytical method for a discussion of how the extract will be stored if not immediately analyzed.
(2) Volumes of surrogates and matrix spiking are logged in the laboratory standard log book

QAPP Worksheet #24
Analytical Instrument Calibration

INSTRUMENT	CALIBRATION PROCEDURE	FREQUENCY OF CALIBRATION	ACCEPTANCE CRITERIA	CORRECTIVE ACTION (CA)	PERSON RESPONSIBLE FOR CA	SOP REFERENCE[1]
Cold Vapor Atomic Fluorescence Spectrometer (CVAFS)	See C-4 C 7	At the beginning of each analysis sequence	See C-4 C 7	Correct the problem and repeat the calibration	Analyst	C-4 C 7
ICPMS	See W 14 W 26	At the beginning of each analysis sequence CCV analyzed after calibration after every 10 samples (max) and at end. Initial calibration blank/verification follow first CCV	See W 14 W 26	Inspect the instrument, correct problems repeat calibration	Analyst	W 14 W 26
GC/MS	Tuning See C 5 W 15 & W 21	Before 12 hr sample analysis	See C 5 W 15 & W 21	Inspect the instrument, correct problems re tune and/or recalibrate	Analyst	See C 5 W 15 & W 21
	Calibration, See C 5 W 15 & W 21	Initial calibration at instrument set up and when calibration verification or tuning fail criteria Calibration verification before 12 hr sample analysis	See C 5 W 15 & W 21	Inspect the instrument, correct problems and recalibrate	Analyst	See C 5 W 15 & W 21

QAPP Worksheet #24
Analytical Instrument Calibration

INSTRUMENT	CALIBRATION PROCEDURE	FREQUENCY OF CALIBRATION	ACCEPTANCE CRITERIA	CORRECTIVE ACTION (CA)	PERSON RESPONSIBLE FOR CA	SOP REFERENCE[1]
GC/FID	See W 22 & W 23	Initial calibration at instrument set up and when calibration verification fails criteria. Check mid point standards after every 10 samples and at the beginning and end of the analysis	Initial calibration RSD ≤ 20% For continuing calibration standard must not exceed a percent difference of ± 15	Inspect system correct problem, and rerun calibration on affected samples	Analyst	See W 22 & W 23
GC/ECD	See W 1 W-4 & C 13	After initial calibration, a check standard of the match point Aroclor 1016/1260 mixture is analyzed after every 10 samples and at the end of the sequence	Initial calibration RSD for 1016/1260 ≤ 20% or linear regression >0 99 Continuing calibration standard must not exceed a percent difference of ± 15	Inspect system, correct problem, and rerun calibration on affected samples	Analyst	See W 1 W-4 & C 13
Balance	See SOP W 5 & C 16	Daily	NA	Inspect system, correct problem and rerun calibration on affected samples	Analyst	W 2 W 5 and C 16

QAPP Worksheet #24
Analytical Instrument Calibration

INSTRUMENT	CALIBRATION PROCEDURE	FREQUENCY OF CALIBRATION	ACCEPTANCE CRITERIA	CORRECTIVE ACTION (CA)	PERSON RESPONSIBLE FOR CA	SOP REFERENCE[1]
Flow Injection Analyzer	See SOP C 8 C 9	Initial calibration at instrument set up and when calibration verification fails criteria. Verification checked with blank and three standards at the beginning of the analysis Analyze continuing calibration standard after every 10 samples and at end of sequence	See SOP C 8 and C 9	Inspect system, correct problem and rerun calibration on affected samples	Analyst	C 8 C 9
Spectrophotometer	Construct two 6-point calibration curves of absorbance versus concentration for low and high levels (one curve for Phosphorus)	Before sample analysis when check standard is outside Confidence Limits also after major instrument maintenance	See SOPs W 3 W 24 C 10	Fix problem and recalibrate	Analyst	W 3 W 24 C 10

Footnote
[1]See Analytical SOP References (Worksheet #23)

QAPP Worksheet #25
Analytical Instrument and Equipment Maintenance, Testing, and Inspection

INSTRUMENT/ EQUIPMENT	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
GC/ECD	▪ Change septa weekly or as needed. ▪ Change gas line dryers as needed. ▪ Replace injection port liner weekly or as needed. ▪ Clip column. ▪ Replace GC column as needed. ▪ Clean/Replace detector as needed. ▪ Provide that gas supply is sufficient and delivery pressure is adequate	Conduct leak test.	Check connections and bake out instrument.	W 1 W-4 and C 13	W 1 W-4 and C-13	Inspect system, correct problem, rerun calibration and reanalyze affected samples	Analyst	W 1 W-4 and C 13
GC/MS	▪ See W 15 W 21 C 5		See W 15 W 21 C 5	See W 15 W 21 C 5	See W 15 W 21 C 5	Inspect system, correct problem, and rerun calibration on affected samples	Analyst	See W 15 W 21 C 5
GC/FID	▪ See W 22 W 23		See W 22 W 23	See W 22 W 23	See W 22 W 23	Inspect system, correct problem, and rerun calibration on affected samples	Analyst	See W 22 W 23
Spectro photometer	▪ Dust lamp and front of front lens ▪ Clean sample compartment. ▪ Clean windows ▪ Clean cuvettes		Check the zero	Daily	See W 3 W 24 C 10	Inspect system, correct problem, and rerun calibration on affected samples	Analyst	W 3 W 24 C 10
Flow Injection Analyzer	See C 8 and C 9		See C-8 and C 9	See C 8 and C-9	See C 8 and C 9	Inspect system, correct problems re run calibration and affected samples if necessary	Analyst	C 8 and C 9
Balance	▪ Professional service contract		NA	Once/year	NA	NA	Service contractor	NA

QAPP Worksheet #25
Analytical Instrument and Equipment Maintenance, Testing, and Inspection

INSTRUMENT/ EQUIPMENT	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
ICPMS	See ICPMS Instruction Manual		Check gas cylinder pressures recirculator is 20°C allow 30 min warm up after ignition, run performance report, tune instrument	W 14 W 26	W 14 W 26	Inspect system resolve any deficiencies rerun calibration on affected samples	Analyst	W 14 W 26
Cold Vapor Atomic Fluorescence Spectrometer (CVAFS)	See C-4 C 7		See C-4 C 7	See C-4 C 7	See C-4 C 7	Inspect system, correct problems re run calibration and affected samples if necessary	Analyst	C-4 C 7

Notes
(1) See Analytical SOP References (Worksheet #23)

QAPP Worksheet #26
Sample Handling System (WATS/CAS)

SAMPLE COLLECTION PACKAGING AND SHIPMENT
Sample Collection (personnel/organization) Emily Stahl, CRA
Sample Packaging (personnel/organization) Emily Stahl CRA
Coordination of Shipment (personnel/organization) Emily Stahl CRA
Type of Shipment/Carrier Overnight courier
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (personnel/organization) Dennis Catalano WATS (or designee) and/or Jeff Christian (or designee) CAS
Sample Custody and Storage (personnel/organization) Dennis Catalano WATS (or designee) and/or Jeff Christian (or designee) CAS
Sample Preparation (personnel/organization) Dennis Catalano WATS (or designee) and/or Jeff Christian (or designee) CAS
Sample Determinative Analysis (personnel/organization) Dennis Catalano WATS (or designee) and/or Jeff Christian (or designee) CAS
SAMPLE ARCHIVING
Field Sample Storage (number of days from sample collection) 30 days from submittal of final report
Sample Extract/Digestate Storage (number of days from extraction/digestion) 60 days from submittal of final report
Biological Sample Storage (number of days from sample collection) NA
SAMPLE DISPOSAL
Personnel/Organization. Dennis Catalano WATS and/or Jeff Christian CAS
Number of Days from Analysis 60 days minimum from submittal of final report

QAPP Worksheet #27
Sample Custody Requirements

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory)

1 The field sampler is personally responsible for the care and custody of the samples until they are transferred to the laboratory or properly dispatched. Keeps the number of people handling the samples to a minimum to ensure proper field Chain-of Custody

2 Field Chain of-Custody Records will accompany all analytical samples and sample shipping containers to document their transfer from the field to the analytical laboratory The procedures to be implemented are as follows

   1 Complete CRA supplied Chain-of-Custody Records Indicating sample identification, containers filled, sampling date sampling time sample collector s name and sample preservation, if applicable Also note this information in the field notebooks

   2 Repack shipping containers with samples Chain-of-Custody Records and water ice Assign a Chain of Custody Record to each set of sample containers to be shipped.

   3 Place completed Chain-of Custody Records in a plastic bag seal the bag and tape it to the inside cover of the shipping container After the samples are iced add the date to the Chain of Custody Record, seal the coolers with strapping tape add custody seals and ship the coolers to WATS Laboratory or subcontractor laboratory (i e CAS) using an overnight delivery service Identify common carriers or intermediate individuals on the Chain-of-Custody Record, and retain copies of all bills-of lading. When the samples are received in the laboratory handle and process them in accordance with laboratory SOPs or specified analytical methods as defined in this QAPP

   4 The laboratory receiving the samples will check shipping containers for completeness of paperwork, broken custody seals damaged sample containers and sample preservation as specified by the analytical method The laboratory s sample management staff will note any problems log the samples into the laboratory and complete the Chain of-Custody Record. The person relinquishing the samples to the facility or agency will request the representative s signature acknowledging sample receipt. If the representative is unavailable or refuses this is to be noted in the Received By space on the Record

   5 Include copies of the Chain of-Custody Record with the analytical data.

3 A separate sample receipt is prepared whenever samples are split with a government agency The receipt is marked to indicate with whom the samples are being split The person relinquishing the samples to the agency should request the agency representative s signature acknowledging sample receipt If the representative is unavailable or refuses this is to be noted on the receipt and in the field notebook.

4 A copy of the Chain-of-Custody Record will accompany the samples to the laboratory The field sampling personnel will retain one copy with the field notes If a Chain of-Custody Record Is damaged in shipment, the field copy will be made available A written statement will be prepared by the person who collected the samples listing the samples that were recorded on the damaged record, and describing when and how the samples were collected. The statement should include information such as field notebook entries regarding the sample This statement is submitted to Field QA Officer and the CRA Project Manager for further action, as necessary

Laboratory Sample Custody Procedures (receipt of samples archiving, disposal)

The laboratory assigns a unique sequentially numbered sample code to each sample received. Laboratory custody procedures for sample receiving and log in, storage tracking and holding time requirements are described in the laboratory s Quality Assurance Manual and in the Laboratory SOPs (see Attachment 1 5)

QAPP Worksheet #27 (*continued*)
Sample Custody Requirements

Sample Identification Procedures

5 Label each bottle with the project number the sample identifier the sample type the sampler's initials and the date and time of sample collection

6 Complete sample labels for each sample and custody seals for each shipment container using waterproof ink, unless prohibited by weather conditions For example a logbook notation would explain that a pencil was used to fill out the sample tag because the ink pen would not function in freezing weather

Chain-of-Custody Procedures

An example CRA Chain-of-Custody Record is shown in Attachment 1 3 The Records should be legibly completed. Errors will be corrected by drawing a single line through the incorrect information and entering the correct information. All corrections are to be initialed and dated by the person making the correction. This procedure applies to words or figures inserted or added to a previously recorded statement

The following information must be included on the Chain-of Custody Record Attachment 1 3

7 Facility name and address project number and sampler identification

8 "The Sample ID No and Description" portion of the Record must be completed for each sample This information includes the Field Sample ID sample date and time and sample depth The sampling time **MUST** also be noted on the sample bottle (except for blind field duplicates where date and time would not be noted on the bottle label or Chain of-Custody Record)

9 The sample container type and number sample matrix, preservative/filtration, and requested analysis must be designated by checking the appropriate box and/or writing the required information.

Sample custody is documented on the lower portion of the Record, and includes the sampler s signature signatures of persons involved in the possession of the sample with dates and times and the date on which the sample was received at the laboratory as described further below

10 ***Relinquished by/Received by*** This part of the Chain-of Custody Record is a record of the individuals who actually had the samples in their custody The spaces must be used in chronological order as the Chain of Custody Record is transferred with the samples

(1) Sampler signs when relinquishing custody
(1) Person accepting custody of samples from sampler signs
(2) Person in (1) must sign when relinquishing custody
(2) (3) These are completed as necessary in the same manner as above

11 ***Sampler*** The person/persons collecting the samples must sign their name and print their name under their signature and record the date and time they relinquish the samples to either the laboratory or the shipper The final signature is that of the person receiving the samples at the laboratory

12 ***Special Instructions*** – The sampler may provide additional information about a sample *e g* if an odor is present, high or low pH etc

13 ***Possible Hazard Identification*** – The sampler may include any known or suspected hazards associated with the samples Sample entry personnel may add information to this section based on communications from the laboratory Project Manager or Supervisor after samples are received Laboratory Team Leaders will use any hazard information to update and advise their analysts before work is started

Note If commercial carriers are used, the name of the carrier any airbill number and the date and time of relinquishing the sample containers are written on the airbill by sample entry or field personnel, and the airbill is attached to the Chain-of-Custody Record

A copy of the Chain-of Custody Record should be returned with the sample results The laboratory service request number should be written on the Chain of Custody Record to facilitate its use during project data entry

QAPP Worksheet #28-1
QC Samples PCBs (Surface Water/Groundwater)

Matrix	Water	Sampling SOP	F 11 F 16	Field Sampling Organization	CRA
Analytical Group	PCBs	Analytical Method/SOP Reference	W 1	Analytical Organization	WATS
Concentration Level	All	Sampler s Name	NA	Number of Sample Locations	As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <20	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	2 per sample	Laboratory control limits	Re extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-2
QC Samples - TSS (Surface Water)

Matrix: Water
Sampling SOP: F 16
Field Sampling Organization: CRA
Analytical Group: TSS
Analytical Method/SOP Reference: W 2, W5
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18)

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <20	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery

QAPP Worksheet #28-3
QC Samples - Phosphorus (Surface Water)

Matrix: Water
Sampling SOP: F 16
Field Sampling Organization: CRA
Analytical Group: Total phosphorus
Analytical Method/SOP Reference: W 3
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <20	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-4
QC Samples - PCBs (Soil/Sediment)

Matrix	Soil/Sediment	Sampling SOP	F-4 F 5 F-6	Field Sampling Organization	CRA
Analytical Group	PCBs	Analytical Method/SOP Reference	W-4	Analytical Organization	WATS
Concentration Level	All	Sampler s Name	NA	Number of Sample Locations	As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <50	Qualify data as needed.	CRA QA Officer	Precision	RPD
Surrogates	2 per sample	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-5
QC Samples: PCBs (Free Product)

Matrix: Free Product
Sampling SOP: F 1 F 3
Field Sampling Organization: CRA
Analytical Group: PCBs
Analytical Method/SOP Reference: C 13
Analytical Organization: CAS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Surrogates	1 per sample	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-6
QC Samples –Metals (Groundwater)

Matrix: Water
Sampling SOP: F 11
Field Sampling Organization: CRA
Analytical Group: Metals
Analytical Method/SOP Reference: W 14
Analytical Organization: WATS
Concentration Level: All (Except Low Level Mercury)
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-7
QC Samples –Metals (Soil/SPLP)

Matrix: Soil
Sampling SOP: F 5 F 6
Field Sampling Organization: CRA
Analytical Group: Metals and SPLP Metals
Analytical Method/SOP Reference: W 14
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-8
QC Samples – Cyanide (Groundwater)

Matrix: Water
Sampling SOP: F 11
Field Sampling Organization: CRA
Analytical Group: Cyanide
Analytical Method/SOP Reference: W 24
Analytical Organization: WATS
Concentration Level: Total
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-9
QC Samples – Cyanide (Soil)

Matrix	Soil	Sampling SOP	F 5 F-6	Field Sampling Organization	CRA
Analytical Group	Cyanide	Analytical Method/SOP Reference	W 24	Analytical Organization	WATS
Concentration Level	Total	Sampler s Name	NA	Number of Sample Locations	As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-10
QC Samples – Low Level Mercury (Surface Water/Groundwater)

Matrix: Water
Sampling SOP: F 11 F 16
Field Sampling Organization: CRA
Analytical Group: Mercury
Analytical Method/SOP Reference: C-4
Analytical Organization: CAS
Concentration Level: Low Level
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Trip blanks	1 per cooler	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-11
QC Samples SVOCs (Groundwater)

Matrix: Water
Sampling SOP: F 11
Field Sampling Organization: CRA
Analytical Group: SVOCs
Analytical Method/SOP Reference: W 15
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	6 per sample	Laboratory control limits	Re extraction/ Re analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-12
QC Samples - SVOCs (Soil)

Matrix: Soil
Sampling SOP: F 5 F 6
Field Sampling Organization: CRA
Analytical Group: SVOCs
Analytical Method/SOP Reference: W 15
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	6 per sample	Laboratory control limits	Re extraction/ Re analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-13
QC Samples - VOCs (Groundwater)

Matrix: Water
Sampling SOP: F 11
Field Sampling Organization: CRA
Analytical Group: VOCs
Analytical Method/SOP Reference: W 21
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	3 per sample	Laboratory control limits	Re analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Trip blank	1 per cooler	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qual fy data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA Data Validator	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-14
QC Samples VOCs (Soil)

Matrix: Soil
Sampling SOP: F 5 F-6
Field Sampling Organization: CRA
Analytical Group: VOCs
Analytical Method/SOP Reference: C 5
Analytical Organization: CAS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	4 per sample	Laboratory control limits	Re analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-15
QC Samples – DRO & GRO (Soil)

Matrix	Soil	Sampling SOP	F 5 F-6	Field Sampling Organization	CRA
Analytical Group	DRO & GRO	Analytical Method/SOP Reference	W 22& W 23	Analytical Organization	WATS
Concentration Level	All	Sampler s Name	NA	Number of Sample Locations	As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	1 per sample (DRO) 2 per sample (GRO)	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory Control Sample (LCS)	1 per analytical batch	Laboratory control limits	Reanalysis	Laboratory Staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-16
QC Samples - Hardness (Surface Water)

Matrix	Water	Sampling SOP	F 16	Field Sampling Organization	CRA
Analytical Group	Hardness (Calculation)	Analytical Method/SOP Reference	W 26	Analytical Organization	WATS
Concentration Level	All	Sampler s Name	NA	Number of Sample Locations	As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <50	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-17
QC Samples – Methyl Mercury (Surface Water/Groundwater)

Matrix: Water
Sampling SOP: F 16 F 11
Field Sampling Organization: CRA
Analytical Group: Methyl Mercury
Analytical Method/SOP Reference: C 7
Analytical Organization: WATS
Concentration Level: Low Level
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 50%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-18
QC Samples - Phosphorus (Soil)

Matrix: Soil
Sampling SOP: F 5, F 6
Field Sampling Organization: CRA
Analytical Group: Total phosphorus (Wet Chemistry)
Analytical Method/SOP Reference: C 10
Analytical Organization: CAS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-19
QC Samples – Ammonia-N (Soil)

Matrix: Soil
Sampling SOP: F 5 F 6
Field Sampling Organization: CRA
Analytical Group: Ammonia N (Wet Chemistry)
Analytical Method/SOP Reference: C 9
Analytical Organization: CAS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28 20
QC Samples – Nitrate-N (Soil)

Matrix: Soil
Sampling SOP: F 5, F 6
Field Sampling Organization: CRA
Analytical Group: Nitrate-N (Wet Chemistry)
Analytical Method/SOP Reference: C 8
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-21
QC Samples – Nitrite-N (Soil)

Matrix: Soil
Sampling SOP: F 5 F-6
Field Sampling Organization: CRA
Analytical Group: Nitrite N (Wet Chemistry)
Analytical Method/SOP Reference: C 8
Analytical Organization: WATS
Concentration Level: All
Sampler s Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #29
Project Documents and Records

SAMPLE COLLECTION DOCUMENTS AND RECORDS	ON-SITE ANALYSIS DOCUMENTS AND RECORDS	OFF-SITE ANALYSIS DOCUMENTS AND RECORDS	DATA ASSESSMENT DOCUMENTS AND RECORDS	OTHER
▪ Field notes ▪ Sampling logs ▪ Chain-of Custody Records ▪ Air bills ▪ Custody seals	▪ Equipment calibration logs ▪ Field data records ▪ Field instrument maintenance logs	▪ Sample receipt, custody and tracking records ▪ Standard traceability logs ▪ Equipment calibration logs ▪ Sample prep logs ▪ Run logs ▪ Equipment maintenance testing and inspection logs ▪ Corrective action forms ▪ Reported field sample results ▪ Reported results for standards QC checks and QC samples ▪ Instrument printouts (raw data) for field sample standards, QC checks and QC sample ▪ Data package completeness checklists ▪ Sample disposal records ▪ Extraction/Cleanup records ▪ Raw data (stored on diskette or CD R) ▪ Analytical reports	▪ Data validation checklists ▪ Data quality assessments	▪ Consent Decree documents ▪ Progress reports to the U S EPA ▪ Work plans and Field Sampling Plans ▪ Health and Safety Plans ▪ Quality Assurance Project Plan ▪ Quality Management Plan ▪ Remedial Investigation and Risk Assessment Reports ▪ Feasibility Studies ▪ Design Reports ▪ Construction Documentation Reports ▪ Monitoring Reports

QAPP Worksheet #30
Analytical Services

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	SAMPLE LOCATIONS/ ID NUMBERS	ANALYTICAL SOP	DATA PACKAGE TURNAROUND TIME	LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)	BACKUP LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)
Groundwater Surface water SPLP Leachate	PCBs, TSS Phosphorus Metals/SPLP metals Total Cyanide, SVOCs VOCs Hardness	All	TBD	W 1 W 2 W 5 W 3 W 14 W 24 W 15 W 21 W 26	Standard turnaround time (21 calendar days)	Weyerhaeuser Analysis and Testing Services (WATS) Weyerhaeuser Company Mail Stop WTC2F25 32901 Weyerhaeuser Way Federal Way WA 98001 Dennis Catalano 253 924 6242	TestAmerica, Laboratories Inc 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456 9396
Surface water	Mercury (low level) Methyl Mercury	All	TBD	C-4 C 7	Standard turnaround time (21 calendar days)	Columbia Analytical Services (CAS) Inc 1317 South 13th Avenue Kelso WA 98626 Jeff Christian 360 557 7222	TestAmerica, Laboratories, Inc 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456 9396
Free Product	PCBs Specific Gravity	All	TBD	C 13 C 16	Standard turnaround time (2 calendar days)	Columbia Analytical Services (CAS) Inc 1317 South 13th Avenue Kelso WA 98626 Jeff Christian 360 557 7222	TestAmerica, Laboratories Inc 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456-9396

QAPP Worksheet #30
Analytical Services

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	SAMPLE LOCATIONS/ ID NUMBERS	ANALYTICAL SOP	DATA PACKAGE TURNAROUND TIME	LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)	BACKUP LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)
Soil/ Sediment	PCBs Metals SVOCs DRO/GRO Cyanide Phosphorous Ammonia N Nitrate-N Nitrite N	All	TBD	W-4 W 14 W 15 W 22/W 23 W 25 C 10 C 9 C 8 C 8	Standard turnaround time (21 calendar days)	Weyerhaeuser Analysis and Testing Services (WATS) Weyerhaeuser Company Mail Stop WTC2F25 32901 Weyerhaeuser Way Federal Way WA 9800 Dennis Catalano 253 924 6242	TestAmerica, Laboratories Inc 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456 9396
	VOCs	All	TBD	C 5 C-6	Standard turnaround time (21 calendar days)	Columbia Analytical Services (CAS) Inc 1317 South 13th Avenue Kelso WA 98626 Jeff Christian 360 557 7222	TestAmerica, Laboratories Inc 4101 Shuffel Street NW North Canton OH 44720 Denise Heckler (800) 456-9396
Independent Data Validation	All	All	--	All	--	Conestoga Rovers & Associates 14496 Sheldon Rd Suite 200 Plymouth, MI 48170 Paul Wiseman 734 453 5123	

Notes
NA = not applicable
TBD = to be determined

QAPP Worksheet #31-4
Planned Project Assessments
Plainwell Mill Phase II RI Work Plan

ASSESSMENT TYPE	FREQUENCY	INTERNAL OR EXTERNAL	ORGANIZATION PERFORMING ASSESSMENT	PERSON(S) RESPONSIBLE FOR PERFORMING ASSESSMENT (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR RESPONDING TO ASSESSMENT FINDINGS (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR IDENTIFYING AND IMPLEMENTING CORRECTIVE ACTIONS (CA) (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR MONITORING EFFECTIVENESS OF CA (title and organizational affiliation)
Field performance audit	Periodic based on field schedule	Internal	CRA	Gregory Carli CRA (Project Manager)	Emily Stahl CRA (Project Coordinator)	Golnoush Bolourani CRA (Field QA Officer)	Emily Stahl, CRA (Project Coordinator)
Field systems audit	Periodic based on field schedule	Internal	CRA	Paul Wiseman CRA (QA Officer)	Emily Stahl CRA (Project Coordinator)	Golnoush Bolourani CRA (Field QA Officer)	Emily Stahl, CRA (Project Coordinator)
Laboratory audit	As needed, based on laboratory performance	Internal	CRA	Paul Wiseman CRA (QA Officer)	Dennis Catalano WATS (Laboratory Manager)	Dennis Catalano WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	As needed, based on laboratory performance	Internal	CRA	Paul Wiseman CRA (QA Officer)	Jeff Christian CAS (Laboratory Manager)	Jeff Christian CAS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	Per laboratory QA Plan	Internal	WATS	Dennis Catalano WATS (Laboratory Manager)	Dennis Catalano WATS (Laboratory Manager)	Dennis Catalano WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	Per laboratory QA Plan	Internal	CAS	Jeff Christian CAS (Laboratory Manager)	Jeff Christian CAS (Laboratory Manager)	Jeff Christian CAS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)

QAPP Worksheet #31 5
Planned Project Assessments
12th Street Landfill RA Work Plan

ASSESSMENT TYPE	FREQUENCY	INTERNAL OR EXTERNAL	ORGANIZATION PERFORMING ASSESSMENT	PERSON(S) RESPONSIBLE FOR PERFORMING ASSESSMENT (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR RESPONDING TO ASSESSMENT FINDINGS (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR IDENTIFYING AND IMPLEMENTING CORRECTIVE ACTIONS (CA) (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR MONITORING EFFECTIVENESS OF CA (title and organizational affiliation)
Field performance audit	Periodic based on field schedule	Internal	CRA	Gregory Carli CRA (Project Manager)	Jodie Dembowske CRA (Project Coordinator)	Golnoush Bolourani, CRA (Field QA Officer) and Wayne Bauman, CRA (Construction Manager)	Jodie Dembowske CRA (Project Coordinator)
Field systems audit	Periodic based on field schedule	Internal	CRA	Paul Wiseman CRA (QA Officer)	Jodie Dembowske CRA (Project Coordinator)	Golnoush Bolourani CRA (Field QA Officer) and Wayne Bauman, CRA (Construction Manager)	Jodie Dembowske CRA (Project Coordinator)
Laboratory audit	As needed, based on laboratory performance	Internal	CRA	Paul Wiseman CRA (QA Officer)	Dennis Catalano WATS (Laboratory Manager)	Dennis Catalano WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	As needed, based on laboratory performance	Internal	CRA	Paul Wiseman CRA (QA Officer)	Jeff Christian, CAS (Laboratory Manager)	Jeff Christian, CAS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)

QAPP Worksheet #31-5
Planned Project Assessments
12th Street Landfill RA Work Plan

ASSESSMENT TYPE	FREQUENCY	INTERNAL OR EXTERNAL	ORGANIZATION PERFORMING ASSESSMENT	PERSON(S) RESPONSIBLE FOR PERFORMING ASSESSMENT (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR RESPONDING TO ASSESSMENT FINDINGS (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR IDENTIFYING AND IMPLEMENTING CORRECTIVE ACTIONS (CA) (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR MONITORING EFFECTIVENESS OF CA (title and organizational affiliation)
Laboratory audit	Per laboratory QA Plan	Internal	WATS	Dennis Catalano WATS (Laboratory Manager)	Dennis Catalano WATS (Laboratory Manager)	Dennis Catalano WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	Per laboratory QA Plan	Internal	CAS	Jeff Christian, CAS (Laboratory Manager)	Jeff Christian, CAS (Laboratory Manager)	Jeff Christian, CAS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)

QAPP Worksheet #32-3
Assessment Findings and Corrective Action Responses
Plainwell Mill Phase II RI Work Plan

ASSESSMENT TYPE	NATURE OF DEFICIENCIES DOCUMENTATION	INDIVIDUAL(S) NOTIFIED OF FINDINGS (name, title, organization)	TIME FRAME OF NOTIFICATION	NATURE OF CORRECTIVE ACTION RESPONSE DOCUMENTATION	INDIVIDUAL(S) RECEIVING CORRECTIVE ACTION RESPONSE (name, title, organization)	TIME FRAME FOR RESPONSE
Field performance audit	Checklist	Emily Stahl CRA (Project Coordinator) will notify Gregory Carli, CRA (Project Manager)	Within 72 hours after audit (or sooner as appropriate)	E mail response	Golnoush Bolourani CRA (Field QA Officer)	Within 48 hours after notification (or sooner as appropriate)
Field systems audit	Checklist	Paul Wiseman, CRA (QA Officer) will notify Gregory Carli CRA (Project Manager)	Within 48 hours after audit (or sooner as appropriate)	E mail response	Golnoush Bolourani CRA (Field QA Officer)	Within 48 hours after notification (or sooner as appropriate)
Internal laboratory audit	Executive Summary from Management Report	Dennis Catalano WATS (Laboratory Manager), will notify Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after audit (or sooner as appropriate)	Executive Summary from Management Report	Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after notification (or sooner as appropriate)
External laboratory audit	Checklist	Paul Wiseman, CRA (QA Officer) will notify Dennis Catalano WATS (Laboratory Manager) and Gregory Carli (Project Manager)	Within 1 week after audit	Memorandum	Dennis Catalano WATS (Laboratory Manager)	Within 48 hours after notification (or sooner as appropriate)

QAPP Worksheet #32-3
Assessment Findings and Corrective Action Responses
Plainwell Mill Phase II RI Work Plan

ASSESSMENT TYPE	NATURE OF DEFICIENCIES DOCUMENTATION	INDIVIDUAL(S) NOTIFIED OF FINDINGS (name, title, organization)	TIME FRAME OF NOTIFICATION	NATURE OF CORRECTIVE ACTION RESPONSE DOCUMENTATION	INDIVIDUAL(S) RECEIVING CORRECTIVE ACTION RESPONSE (name, title, organization)	TIME FRAME FOR RESPONSE
Internal laboratory audit	Executive Summary from Management Report	Jeff Christian, CAS (Laboratory Manager) will notify Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after audit (or sooner as appropriate)	Executive Summary from Management Report	Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after notification (or sooner as appropriate)
External laboratory audit	Checklist	Paul Wiseman, CRA (QA Officer) will notify Jeff Christian, CAS (Laboratory Manager) and Gregory Carli (Project Manager)	Within 1 week after audit	Memorandum	Jeff Christian, CAS (Laboratory Manager)	Within 48 hours after notification (or sooner as appropriate)

QAPP Worksheet #32-4
Assessment Findings and Corrective Action Responses
12th Street Landfill RA Work Plan

ASSESSMENT TYPE	NATURE OF DEFICIENCIES DOCUMENTATION	INDIVIDUAL(S) NOTIFIED OF FINDINGS (name, title, organization)	TIME FRAME OF NOTIFICATION	NATURE OF CORRECTIVE ACTION RESPONSE DOCUMENTATION	INDIVIDUAL(S) RECEIVING CORRECTIVE ACTION RESPONSE (name, title, organization)	TIME FRAME FOR RESPONSE
Field performance audit	Checklist	Jodie Dembowske CRA (Project Director) will notify Gregory Carli, CRA (Project Manager)	Within 72 hours after audit (or sooner as appropriate)	E mail response	Golnoush Bolourani CRA (Field QA Officer) and Wayne Bauman, CRA (Construction Manager)	Within 48 hours after notification (or sooner as appropriate)
Field systems audit	Checklist	Paul Wiseman, CRA (QA Officer) will notify Gregory Carli CRA (Project Manager)	Within 48 hours after audit (or sooner as appropriate)	E mail response	Golnoush Bolourani CRA (Field QA Officer) and Wayne Bauman, CRA (Construction Manager)	Within 48 hours after notification (or sooner as appropriate)
Internal laboratory audit	Executive Summary from Management Report	Dennis Catalano WATS (Laboratory Manager) will notify Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after audit (or sooner as appropriate)	Executive Summary from Management Report	Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after notification (or sooner as appropriate)
External laboratory audit	Checklist	Paul Wiseman, CRA (QA Officer) will notify Dennis Catalano WATS (Laboratory Manager) and Gregory Carli (Project Manager)	Within 1 week after audit	Memorandum	Dennis Catalano WATS (Laboratory Manager)	Within 48 hours after notification (or sooner as appropriate)

QAPP Worksheet #32-4
Assessment Findings and Corrective Action Responses
12th Street Landfill RA Work Plan

ASSESSMENT TYPE	NATURE OF DEFICIENCIES DOCUMENTATION	INDIVIDUAL(S) NOTIFIED OF FINDINGS (name, title, organization)	TIME FRAME OF NOTIFICATION	NATURE OF CORRECTIVE ACTION RESPONSE DOCUMENTATION	INDIVIDUAL(S) RECEIVING CORRECTIVE ACTION RESPONSE (name, title, organization)	TIME FRAME FOR RESPONSE
Internal laboratory audit	Executive Summary from Management Report	Jeff Christian, CAS (Laboratory Manager) will notify Paul Wiseman, CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after audit (or sooner as appropriate)	Executive Summary from Management Report	Paul Wiseman CRA (QA Officer) and appropriate laboratory staff	Within 48 hours after notification (or sooner as appropriate)
External laboratory audit	Checklist	Paul Wiseman, CRA (QA Officer) will notify Jeff Christian, CAS (Laboratory Manager) and Gregory Carli (Project Manager)	Within 1 week after audit	Memorandum	Jeff Christian, CAS (Laboratory Manager)	Within 48 hours after notification (or sooner as appropriate)

QAPP Worksheet #33
QA Management Reports

TYPE OF REPORT	FREQUENCY (daily weekly monthly quarterly annually etc.)	PROJECTED DELIVERY DATE(S)	PERSON(S) RESPONSIBLE FOR REPORT PREPARATION (title and organizational affiliation)	REPORT RECIPIENT(S) (title and organizational affiliation)
Field audit reports	As needed	As generated	Gregory Carli CRA (Project Manager) Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchn (CRA Project Director)
WATS audit (external)	As needed	As generated	Paul Wiseman CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carli (Project Manager)
CAS audit (external)	As needed	As generated	Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carli (Project Manager)
Data validation reports	As specified in data assessment section	As generated	Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carli (Project Manager)

QAPP Worksheet #33
QA Management Reports

TYPE OF REPORT	FREQUENCY (daily weekly monthly, quarterly annually etc.)	PROJECTED DELIVERY DATE(S)	PERSON(S) RESPONSIBLE FOR REPORT PREPARATION (title and organizational affiliation)	REPORT RECIPIENT(S) (title and organizational affiliation)
Data quality summary	As appropriate for data use	As generated	Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carli (Project Manager)

QAPP Worksheet #34
Verification (Step I) Process

VERIFICATION INPUT	DESCRIPTION	INTERNAL/ EXTERNAL	RESPONSIBLE FOR VERIFICATION (name organization)
Chain-of-Custody Records and shipping documentation	Chain-of Custody Records and shipping documentation will be reviewed by the laboratory upon receipt of samples for verification against the sample coolers they represent. The Chain-of-Custody Record will be signed by all parties who had custody of samples with the exception of commercial carriers	Internal	Dennis Catalano WATS (or designee) (Laboratory Manager) and/or Jeff Christian CAS (or designee) (Laboratory Manager)
Field notes and sampling logs	All field notes and sampling logs will be reviewed internally and placed in the project file	Internal	Emily Stahl CRA (Project Coordinator)
Laboratory data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal.	Internal	Dennis Catalano WATS (or designee) (Laboratory Manager)
Laboratory data	All final data packages will be verified for content upon receipt.	Internal	Paul Wiseman, CRA (QA Officer)

QAPP Worksheet #35
Validation (Step I) Process

STEP IIa/IIb	VALIDATION INPUT	DESCRIPTION	RESPONSIBLE FOR VERIFICATION (Name, Organization)
Step IIa	Sampling methods and procedures	Verify that the required analytical methods were used and that any deviations were noted.	Paul Wiseman, CRA
Step IIa	Analytical methods	Verify that the required sampling methods were used and that any deviations were noted The laboratory will verify that QC samples met the performance criteria, and that any deviations were noted on the sample narrative	Dennis Catalano WATS Jeff Christian, CAS Paul Wiseman, CRA
Step IIb	Documentation of QAPP QC sample results	Establish that all QC samples required by the QAPP were collected and analyzed.	Paul Wiseman, CRA
Step IIb	Project Quantitation Limits	Determine that the QAPP required Quantitation Limits were achieved.	Paul Wiseman, CRA
Step IIb	Validation report	Summarize data findings of verification and validation components included in the QAPP Include comments on any qualified data, and define all qualifiers	Paul Wiseman, CRA

QAPP Worksheet #36
Validation (Steps IIa and IIb) Summary

STEPS IIa AND IIb	MATRIX	ANALYTICAL GROUP	DATA PURPOSE	CONCENTRATION LEVEL	VALIDATION CRITERIA	DATA VALIDATOR (title and organizational affiliation)
IIa and IIb	Soil/ Sediment	PCBs, VOCs PAHs/SVOCs	Site Investigation, Remedial Design, or Confirmation of Remediation, Remedial Investigation, Remedial Action	Low medium, high	U S EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (October 1999) method and laboratory SOP criteria, QAPP criteria, and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Soil/ Sediment	Metals, Cyanide Low Level Mercury Methyl Mercury	Site Investigation, Remedial Design, or Confirmation of Remediation, Remedial Investigation, Remedial Action	Low medium, high	U S EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (February 1994/ October 2004) method and laboratory SOP criteria, QAPP criteria, and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Water	PCBs VOCs PAHs/SVOCs	Site Investigation, Remedial Design, Confirmation of Remediation, Remedial Investigation, Remedial Action, or Long Term Monitoring	Low medium, high	U S EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (October 1999) method and laboratory SOP criteria, QAPP criteria, and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Water	Metals Cyanide Low Level Mercury Methyl Mercury	Site Investigation, Remedial Design Confirmation of Remediation, Remedial Investigation Remedial Action, or Long Term Monitoring	Low medium, high	U S EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (February 1994/ October 2004) method and laboratory SOP criteria, QAPP criteria, and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Oil	PCBs & Specific Gravity	Site Investigation, Remedial Action	Low medium, high	U S EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (October 1999) method and laboratory SOP criteria, QAPP criteria, and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Aqueous/ Soil/ Sediment	General chemistry parameters	Confirmation of remediation, Remedial Investigation, Remedial Action	Low medium, high	U S EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (February 1994) method and laboratory SOP criteria, QAPP criteria, and professional judgment	Paul Wiseman (CRA)

QAPP Worksheet #37
Usability Assessment

Identify the personnel responsible for performing the usability assessment
Conestoga Rovers & Associates (CRA) will perform the usability assessment for analytical data. Paul Wiseman is responsible for data validation at CRA The CRA Project Coordinator is responsible for verification of field activities The CRA Project Manager CRA Project Coordinator and CRA QA Officer will determine if field and analytical data or datasets meet the requirements necessary for decision making The results of these measurements will be compared with the DQO requirements set forth in this QAPP As data are evaluated, anomalies in the data or data gaps may become apparent to the data users The DQOs will be satisfied if the data are sufficient (based on the quality and completeness of the data) to meet the project objectives Data that do not meet the data users needs (if any) will be identified and appropriately qualified in the project database so that the decision makers are aware of the limitations
Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used
The Data Reviewer will review field notes and field Chain-of-Custody Records to determine that procedures specified in the FSP have been followed. Validation of the analytical data will be performed by CRA chemistry staff at the direction of CRA s QA Officer based on the relevant and applicable evaluation criteria outlined in "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review EPA 540/R 99/008 October 1999 and "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" EPA 540/R 94-013 February 1994 The elements reviewed, objectives established, evaluation approach, and actions taken will be as specified in these documents (referred to hereafter as NFGs) for the data quality assessment and validation. The specific criteria used will be as defined in the NFGs with the exception of the acceptance limits for the lab QC samples (surrogates matrix spike/matrix spike duplicates and laboratory control samples) which are either statistically determined by the laboratory as specified by the analytical methods and/or the specific control limits defined by the analytical methods and laboratory SOPs specified in this QAPP The holding times blanks instrument performance checks initial calibration, continuing calibration, internal standards and serial dilutions requirements will be evaluated as specified in the NFGs where applicable with select criteria for ICP MS evaluation from "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" EPA 540/R-04-004 October 2004 Data validation will determine whether the procedures specified in the FSP and in this QAPP were implemented, the DQOs specified in this QAPP were attained, the specified Quantitation Limits were achieved, and the sample holding times were met. An evaluation of data accuracy precision, sensitivity and completeness based on method specific criteria, will be performed according to the validation protocols presented above All forms will be checked. A representative portion (10 percent) of the sample raw data, including chromatograms quantitation reports data system printouts and mass spectra will be randomly selected and reviewed. A portion (~10 percent) of calculations such as spike recoveries calibration response factors analyte quantitation, etc will be randomly spot checked.

QAPP Worksheet #37
Usability Assessment

The procedures used to evaluate data include the following

- All technical holding times will be checked for inorganic and organic analyses
- Instrument performance check sample results, and initial and continuing calibration results will be evaluated
- Data for all blanks surrogate spikes matrix spikes/matrix spike duplicates laboratory control samples cleanup standards internal and external standards target compound identification and quantitation, and system performance checks will be reviewed.
- Sample calculations will be checked.
- Field precision will be determined from blind field duplicate data.
- Completeness of the data package will be checked to determine if all samples and analyses required by the QAPP were processed, that the procedures specified in the QAPP were implemented, and that all deliverables specified in the QAPP are included.
- The Data Reviewer will identify any out-of-control data points and data omissions and will interact with the laboratory to correct data deficiencies
- Decisions to repeat sample collection and analyses may be made by the CRA Project Manager based on the extent of the deficiencies and their importance in the overall context of the project.
- The CRA QA Officer will assess the usability of results against the DQOs

QAPP Worksheet #37 (*continued*)
Usability Assessment

Describe the evaluative procedures used to assess overall measurement error associated with the project

The data quality indicator (DQIs) used to evaluate conformance with the project DQOs are presented below

DQIs are generally defined in terms of the following six parameters

1 Representativeness
2 Comparability
3 Completeness
4 Precision
5 Accuracy
6 Sensitivity

Each parameter is defined below Specific objectives for the site actions are presented in other sections of this QAPP as referenced below

Representativeness

Representativeness is the degree to which sampling data accurately and precisely represent site conditions and is dependent on sampling and analytical variability and the variability of environmental media at the site Actions have been designed to assess the presence of chemical constituents at the time of sampling The QAPP presents the rationale for sample quantities and location. This QAPP presents field sampling and laboratory analytical methodologies Use of the prescribed field and laboratory analytical methods with associated holding times and preservation requirements is intended to provide representative data

Comparability

Comparability is the degree of confidence with which one data set can be compared with another Comparability between phases of the actions (if additional phases are required) will be maintained through consistent use of the sampling and analytical methodologies set forth in the QAPP the established QA/QC procedures and the use of appropriately trained personnel

Completeness

Completeness is defined as a measure of the amount of valid data obtained from an event and/or investigation compared to the total amount that was obtained This will be determined upon final assessment of the analytical results Completeness of a field or laboratory data set will be calculated by comparing the number of valid sample results generated with the total number of results generated.

$$\text{Completeness} = \frac{\text{Number valid results}}{\text{Total number of results generated}} \times 100$$

As a general guideline overall project completeness is expected to be at least 90 percent. The assessment of completeness will require professional judgment to determine data usability for intended purposes

QAPP Worksheet #37 (*continued*)
Usability Assessment

Precision

Precision is a measure of the reproducibility of sample results The goal is to maintain a level of analytical precision consistent with the objectives of the action To maximize precision, sampling and analytical procedures will be followed. All work for the site actions will adhere to the established protocols presented in the QAPP Checks for analytical precision will include the analysis of MS/MSDs, laboratory duplicates and field duplicates Checks for field measurement precision will include duplicate field measurements

The precision of data will be measured by calculating the Relative Percent Difference (RPD) by the following equation

$$RPD = \frac{(A\ B)}{(A+B)/2} \times 100$$

where

A = analytical result from one of two duplicate measurements
B = analytical result from the second measurement.

Accuracy

Accuracy is a measure of how close a measured result is to the true value Both field and analytical accuracy will be monitored through initial and continuing calibration of instruments In addition, reference standards MSs blank spikes and surrogate standards will be used to assess the accuracy of the analytical data

Accuracy will be calculated in terms of percent recovery as follows

$$\%\ Recovery = \frac{A\ X}{B} \times 100$$

where

A = value measured in spiked sample or standard,

X = value measured in original sample

B = true value of amount added to sample or true value of standard.

Sensitivity

Sensitivity is a quantitative measurement to determine if the analytical laboratory s procedures/methodologies and their associated MDLs can satisfy the project requirements as they relate to the project action limits MDLs are updated annually by the laboratory

QAPP Worksheet #37 (*continued*)
Usability Assessment

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations) and anomalies
The data validation report will address the following items ▪ Overall quality and usability of the data ▪ Evaluation of QC data, including precision, accuracy and completeness of the data ▪ Potential sample contamination due to blank contributions ▪ Assessment of laboratory and field records ▪ Actions regarding specific QC criteria exceedences Laboratory applied data qualifiers will be defined within the analytical data package received from the laboratory The sample narrative will also detail quality control issues identified by the laboratory Data validation qualifiers that may be applied to the data include the following U The analyte/compound was analyzed for but not detected. The associated value is the compound s Limit of Quantitation UJ The compound was not detected above the reported sample s Limit of Quantitation However the reported limit is approximate and may or may not represent the actual Limit of Quantitation J The compound was positively identified however the associated numerical value is an estimated concentration only R The sample results are rejected.

ATTACHMENTS

ATTACHMENT 1-3

SAMPLE CHAIN-OF CUSTODY RECORD

CHAIN OF CUSTODY RECORD

COC NO PL-24567

14496 Sheldon Road, Suite #200 Plymouth, Michigan 48170
(734) 453-5123 Fax: (734) 453-5201

PAGE ___ OF ___

CONESTOGA-ROVERS & ASSOCIATES

Project No	Phase/Task Code	Laboratory Name	Lab Location	SSOW No
Project Name		Lab Contact:	Lab Quote No	Cooler No
Project Location				Carrier
Chemistry Contact				Airbill No
Sampler(s)				Date Shipped

Item	Sample I D No. (Containers for each sample may be combined on one line)	Date	Time	Sample Type: Grab	Sample Type: Composite	Matrix: Air / Oil / Waste	Matrix: Water	Matrix: Soil	Matrix: Sediment	Matrix: Other	Container Quantity & Preservation: Unpreserved	H_2SO	HNO_3	HCl	NaOH	Thiosulfate	Methanol/Water (Soil VOC)	EnCores 3x5-g 1x25-g	Other	Analysis Requested												MS/MSD Request	Comments Special Instructions/ Conditions Of Receipt
1																																	
2																																	
3																																	
4																																	
5																																	
6																																	
7																																	
8																																	
9																																	
10																																	
11																																	
12																																	
13																																	
14																																	
15																																	

TAT Required ☐ 1 Day ☐ 2 Days ☐ 3 Days ☐ 1 Week ☐ Standard ☐ Other

Lab Deliverables (Select) ☐ Summary ☐ Expanded ☐ Other ☐ See SSOW

Relinquished By	Company	Date	Time	Received By	Company	Date	Time
1				1			
2.				2.			
3.				3			

Additional Comments

Distribution WHITE – Fully Executed Copy YELLOW – Receiving Laboratory Copy PINK – Shipper GOLDENROD – Sampling Crew

ATTACHMENT 1-5

NEW/REVISED LABORATORY STANDARD OPERATING PROCEDURES [1]

W-15 (WATS SOP AM E 8270) SVOC Analysis (revised SOP to incorporate project defined RLs)
W-25 (WATS SOP AM E 1312) SPLP Preparation method for Metals (new SOP)
W-26 (WATS SOP AM S-2340B) Hardness by Calculation (new SOP)
C-2 (CAS SMO SCOC) Chain of Custody (revised SOP)
C 3 (CAS SOP SMO-GEN) Sample Receiving (revised SOP)
C 4 (CAS SOP MET-1631) Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (revised SOP)
C-7 (CAS SOP MET-1630W) Methyl Mercury - in water (new SOP)
C 8 (CAS GEN-353 2) Nitrate/Nitrite (new SOP)
C 9 (CAS GEN-350 1) Ammonia (new SOP)
C 10 (CAS 365 3) Phosphorous (new SOP)
C-11 (CAS ADM-BAL 1) Balance (new SOP)
C-12 (CAS ADM-CA) Corrective Action (new SOP)
C 13 (CAS SOC 8082Ar) PCBs as Aroclors (revised SOP)
C 14 (CAS EXT 3580) Waste Dilution Extraction (revised SOP)
C-15 (CAS EXT 3665) Sulfuric Acid Cleanup (revised SOP)
C-16 (CAS GEN SPECGRAV) Specific Gravity (revised SOP)

[1] The remainder of SOPs are included in the QAPP Revision 02 Addendum 03 that was submitted by RMT in November 2008

STANDARD OPERATING PROCEDURE

for

SAMPLE TRACKING AND INTERNAL CHAIN-OF-CUSTODY

SOP No SMO-SCOC

UNCONTROLLED

Revision 12

April 23 2009

Approved By _____ Supervisor 4/24/09 Date

_____ QA Manager 4/24/09 Date

COPY

_____ Laboratory Manager 4/27/09 Date

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso Washington 98626

© Columbia Analytical Services Inc 2009

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL

NUMBER _____

Initials _____ Date _____

SAMPLE TRACKING AND INTERNAL CHAIN-OF-CUSTODY

1 PURPOSE

The purpose of this procedure is to maintain and document internal chain of-custody (COC) of samples Custody documentation must be maintained through all phases of analysis - from sample receipt and initial storage to analysis and disposal

2 APPLICABILITY

UNCONTROLLED

The procedure is applicable to all field samples, subsamples, and sample extracts and sample digestates as described in the procedure section

3 DEFINITIONS

3 1 Custody - The guardianship or safe keeping of a sample A sample is considered to be in a person s custody if it is physically in their possession, or it is in their view after being in their possession, or it was in their possession and then locked up or sealed to prevent tampering or it is in a secure area

COPY

3 2 Chain of Custody - The documented order or sequence of the persons having custody of a sample Chain of custody requires that the sample be in custody of some known person from the time it is collected until it is disposed

3 3 Custody record - External or internal COC document that clearly defines and documents who is/was in possession of a sample at a given time

3 4 Login - The SMO process of accepting the sample inspecting and entering the sample information into the laboratory LIMS system

3 5 Sample custodian – The sample management office (SMO) is considered to be the sample custodian for any period of time from sample receipt to sample disposal that the sample is not internally signed into custody by analytical personnel

3 6 Sample tracking Identifying or reproducing the path of sample custody throughout the laboratory

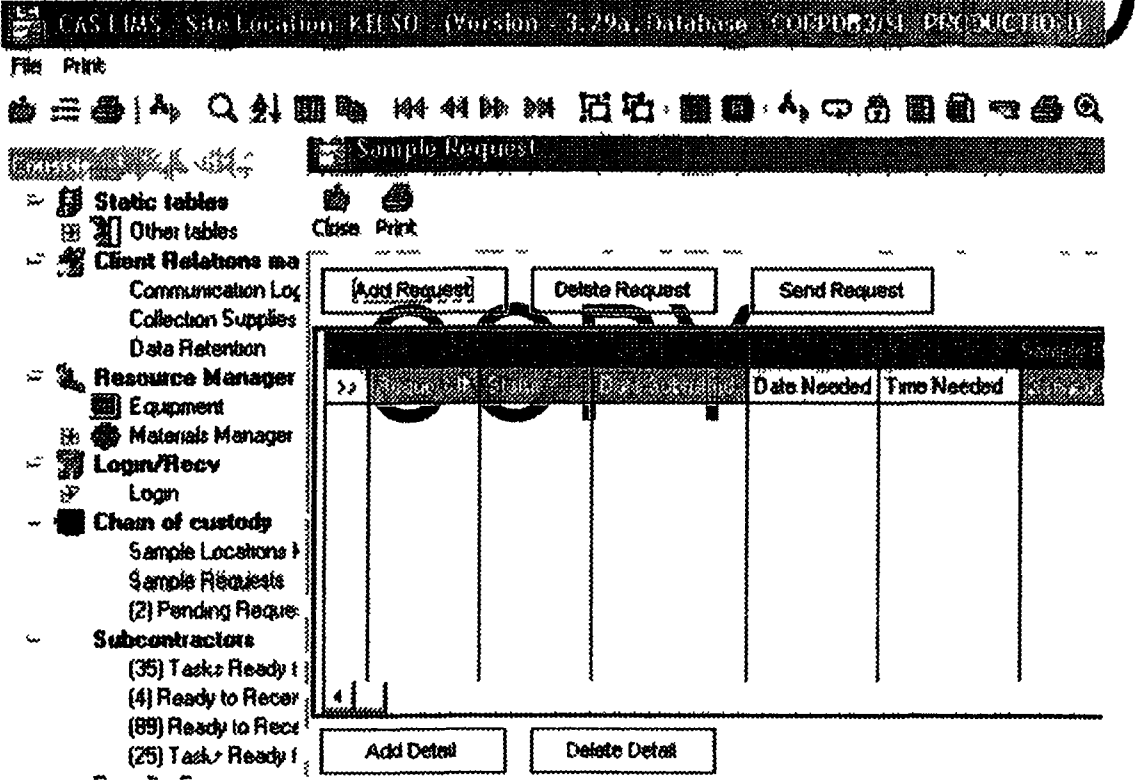
areas the samples are considered to be in the custody of the sample management office (sample custodian) Removal of any sample from the SMO sample storage areas represents a physical change of custody and therefore must be documented via a chain of custody record It is at this point that internal tracking of the samples is initiated

Note All solid samples pulled from a freezer must be placed in a Ziploc storage bag to prevent loss of sample in the event that the jar cracks during thawing

6 2 Requesting Samples through the Sample Custodian

6 2 1 Open the sample request window by clicking on ' Sample Requests under the "Chain of Custody' heading Click the 'Add Request' button

UNCONTROLLED



6 2 2 Enter the necessary information in the Add Request window and click OK.

4 DISCUSSION

Chain of custody is the protocol that provides a record of the persons having control of and access to a sample If the analytical results are questioned the chain of custody documentation is the record that proves the sample was collected and handled according to specification and the sample can be directly linked to the analytical results This is especially important if the analytical results are questioned or to be used in supporting legal proceedings

5 RESPONSIBILITIES

5 1 It is the responsibility of sample custodians and laboratory staff to make sure that the procedures described in this SOP are followed and that chain of custody records are complete and accurate Every appropriate laboratory staff member will be required to familiarize themselves with the procedures listed in this SOP Once the SOP has been read, appropriate supervisory personnel and section managers must ensure that personnel will comply with the procedures listed herein

UNCONTROLLED COPY

5 1 1 **Sample Custodian Responsibilities** It is the responsibility of the Sample Custodian to fill sample requests by the time indicated by the analyst Once the samples are gathered SMO will transfer custody and deliver the samples directly to the requestor Upon return of the samples (within designated business hours) from the analyst, it is the responsibility of SMO to scan the samples back into their home storage location and re-shelve them Samples returned after hours the previous day are to be shelved to their designated shelves by the sample custodians

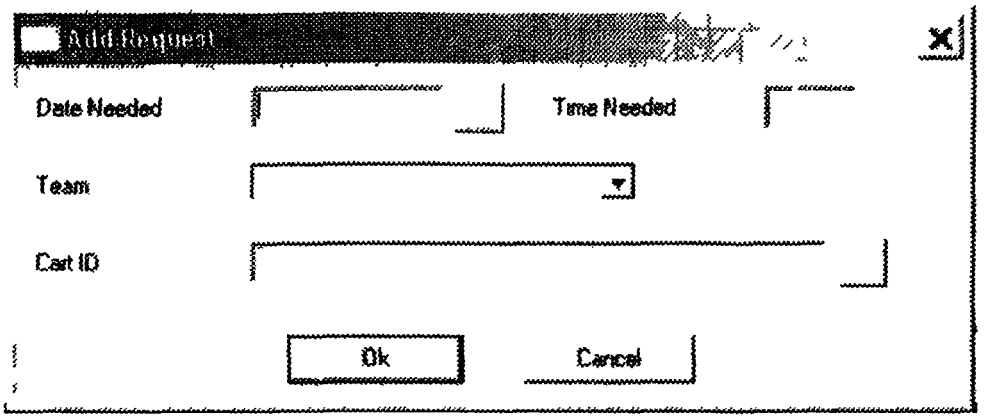
5 1 2 **Analyst Responsibilities** It is the responsibility of the analyst to provide sufficient time for sample requests to be filled by the Sample Custodians It is the responsibility of the analyst to take custody in the LIMS system as soon as they take samples from a storage location Upon completing their work, samples must be returned to the sample storage room as soon as possible to minimize the amount of time samples are held at room temperature

6 PROCEDURES

6 1 Field sample custody

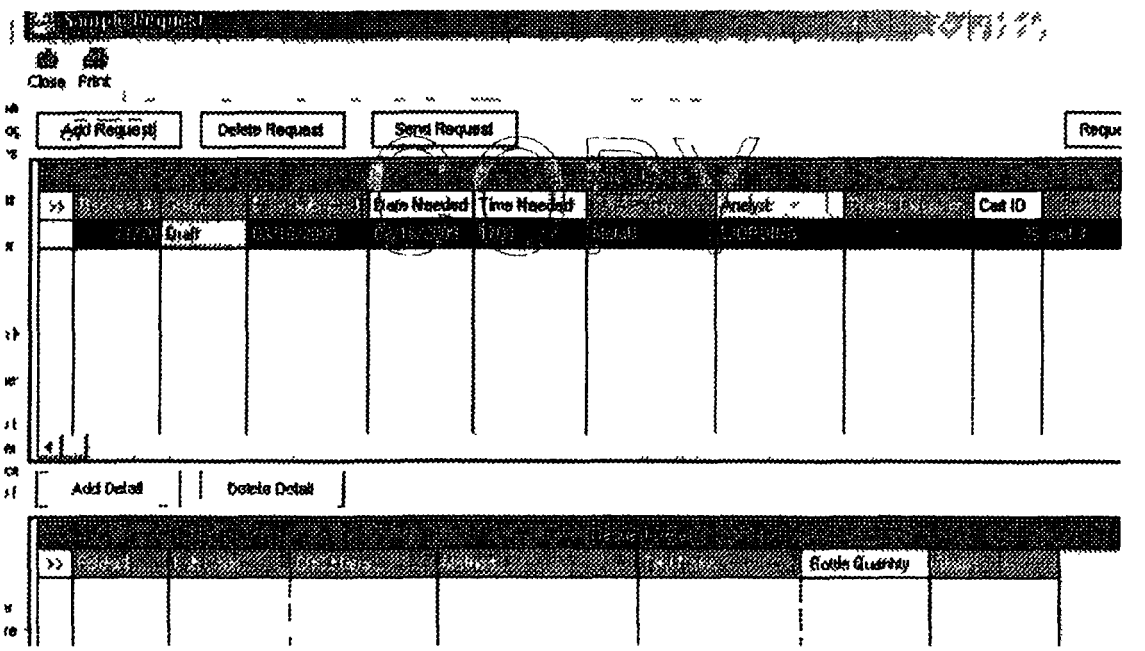
6 1 1 Sample containers are labeled with a bar-code to identify and track field samples throughout the laboratory The bar coding system uses CAS LIMS database for sample information The sample tracking process in the laboratory begins with receipt of samples into the laboratory facility Sample receipt login, identification, labeling, and storage procedures are all described in the SOP SMO-GEN *Sample Receiving* Sample receiving personnel will enter the sample information (Service Request number unique container ID) for each project into the sample database Following login, the samples are placed in the appropriate refrigerator(s)

6 1 2 Access to all samples is controlled Samples are stored in a secure, keypad-locked room or in separate locked storage areas While in these secured and locked storage

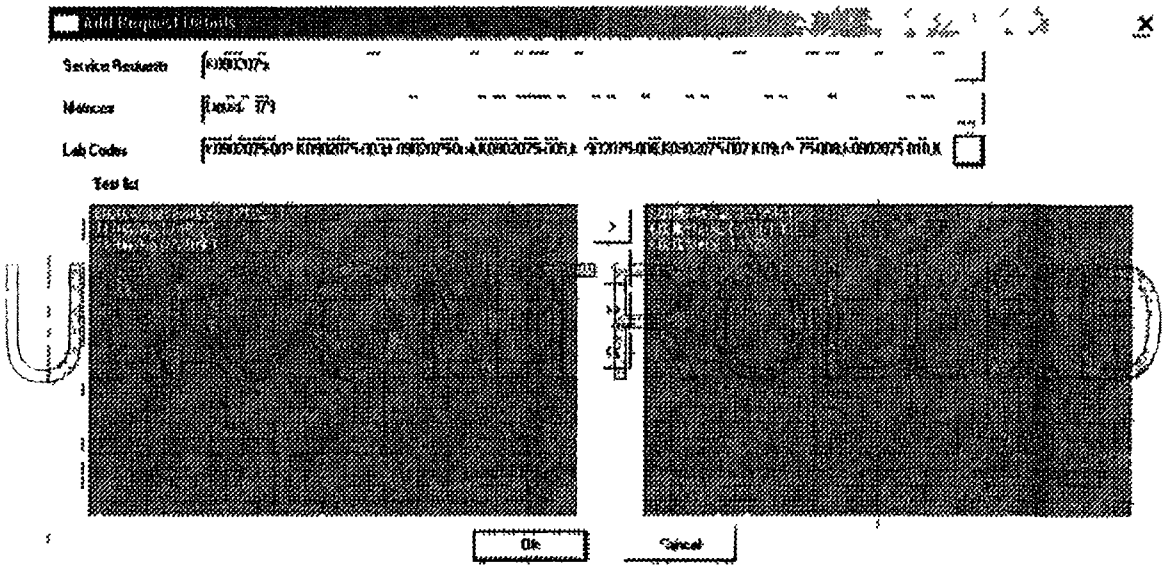


UNCONTROLLED

6 2 3 The sample request screen will appear with the basic information as seen below To add samples to the request click on the ' Add Detail button



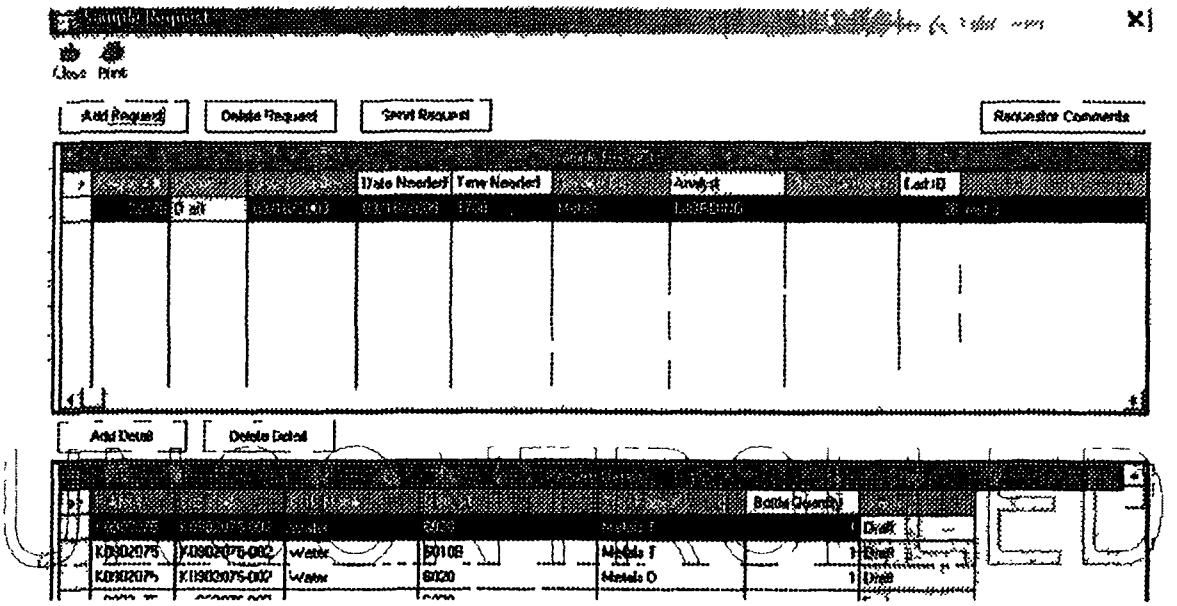
6 2 4 Fill in the details (Service Requests Matrices Lab Codes) and select the tests by highlighting and moving them to the right in the Test List box Click OK



6 2 5 Once all of the samples have been added to the sample request, add any additional information to the request in the ' Requestor Comments ' field (Additional information may include things like specific containers needed, extra volume necessary for QC on a given sample etc) Once the request is complete click the Send Request button

Note If one of your team members will be taking possession of the samples (i e a swing shift team member completes the sample request form but a day crew person will be taking custody of them to begin the testing) double click on the analyst field and change it to the person to whom the samples should be delivered and custody given to

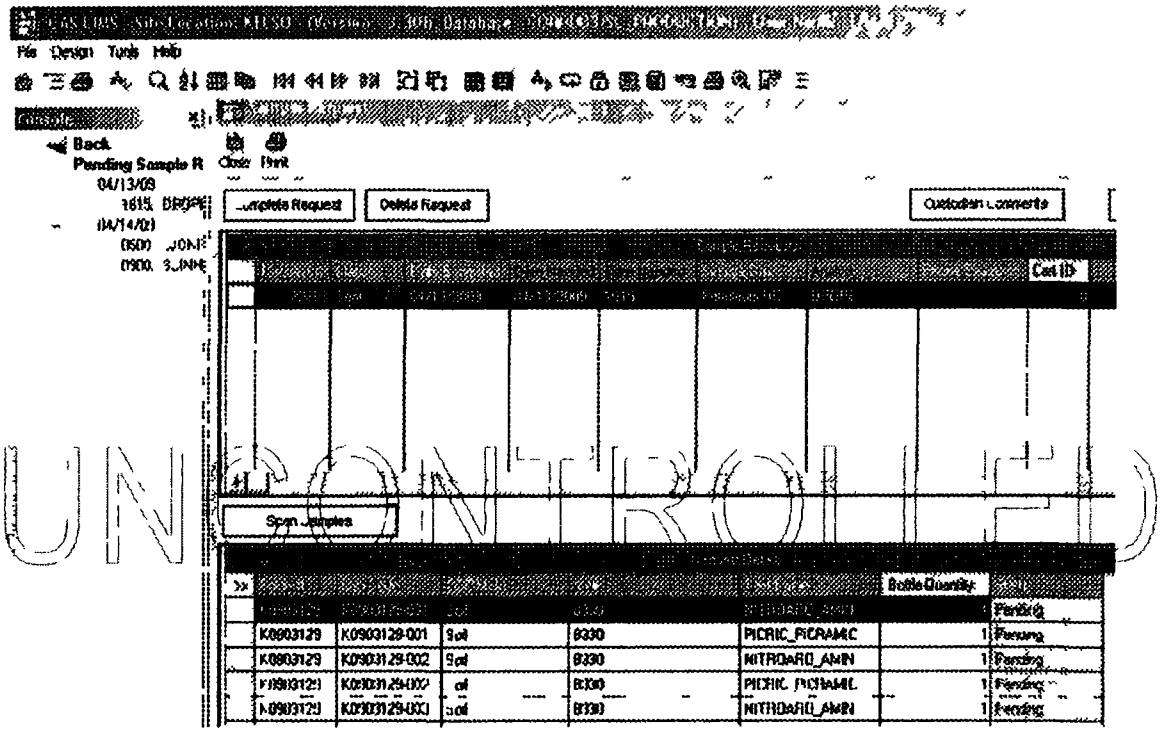
COPY



6 3 The steps to be taken to by SMO to fill a sample request

6 3 1 Under Chain of Custody open up the Pending Requests folder and double click the request The following screen will appear showing the requested list of samples who requested them, and the date and time they are needed Print the request and retrieve the necessary samples

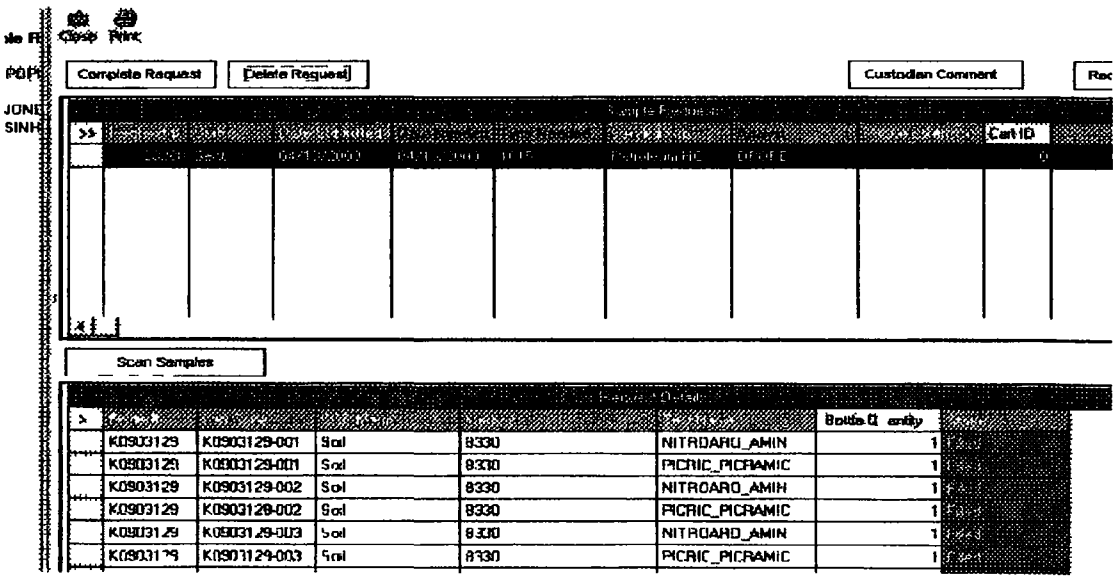
COPY



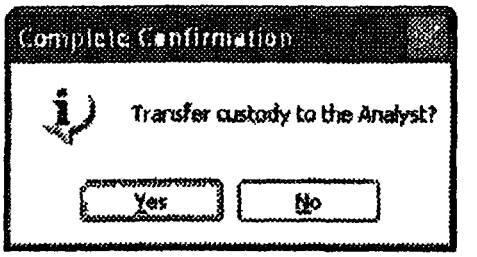
UNCONTROLLED

6 3 2 Click on the Scan Samples button and scan each individual bottle When all bottles are scanned in click the cancel button Review the order to see if any bottles were missed If the samples are not ready to be delivered do not complete the order Place the order in the appropriate refrigerator for delivery at the appropriate time If the order is ready to go to the analyst complete the order by clicking the complete request' button and click Yes

COPY



6 3 3 To finish the order and transfer the custody to the requesting analyst, click ' Yes

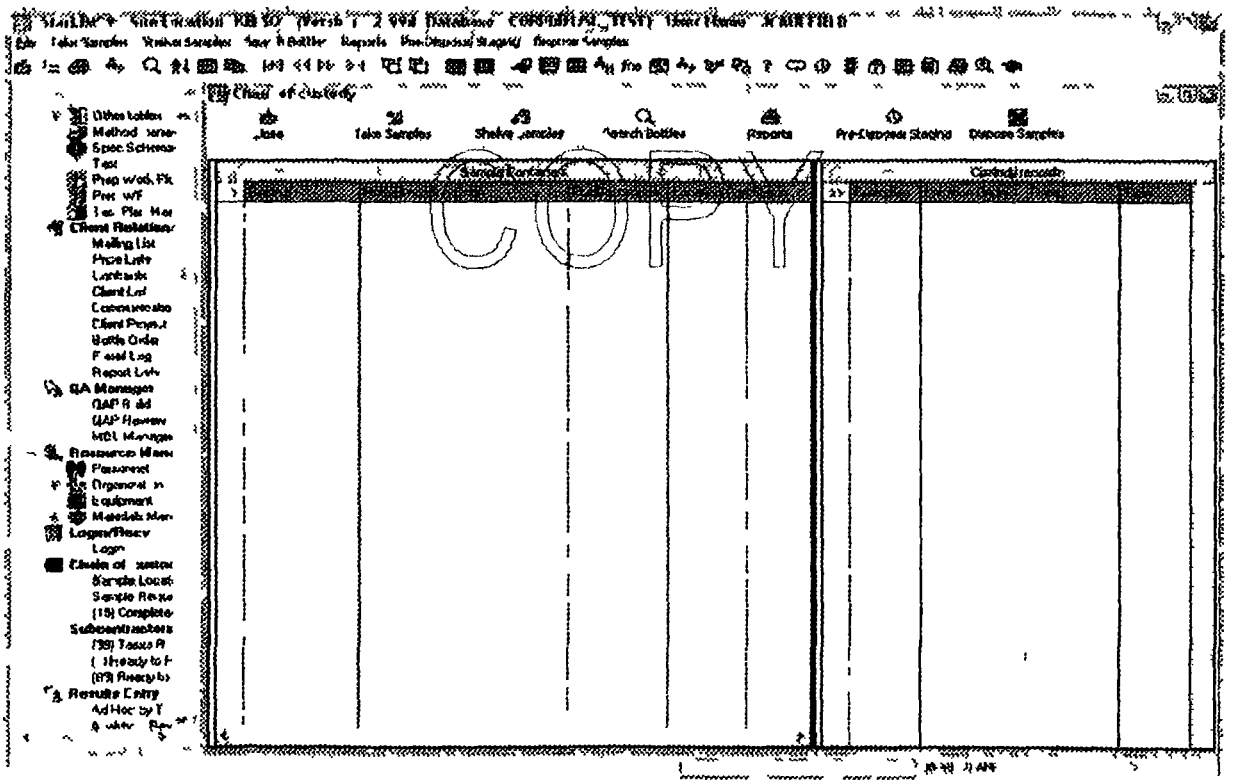


6 3 4 Deliver the samples to the analyst who now has custody of them

UNCONTROLLED

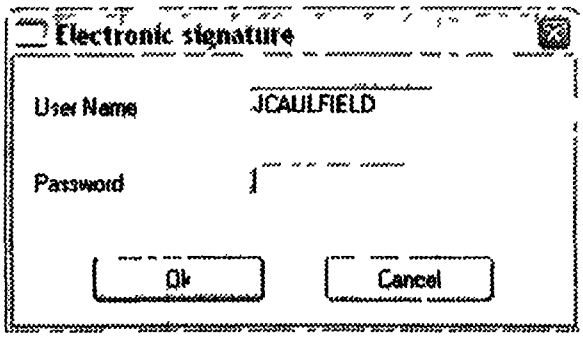
6 4 The steps to be taken to take custody of samples retrieved by an analyst are outlined below

6 4 1 The main menu display on the internal custody workstation appears as follows



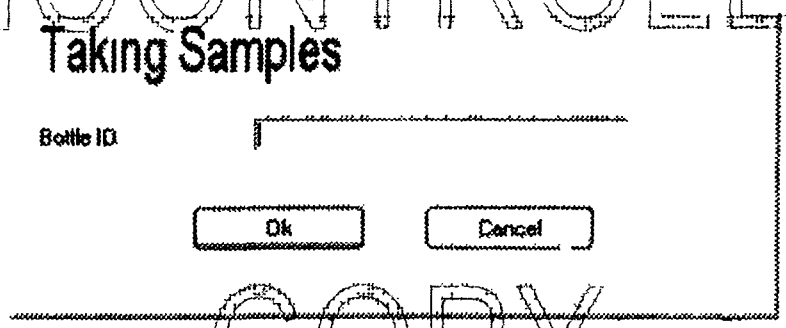
COPY

6 4 2 Choose Take Samples The following Signature window will appear



UNCONTROLLED

6 4 3 Select name from employee list The Taking Samples screen will appear next



COPY

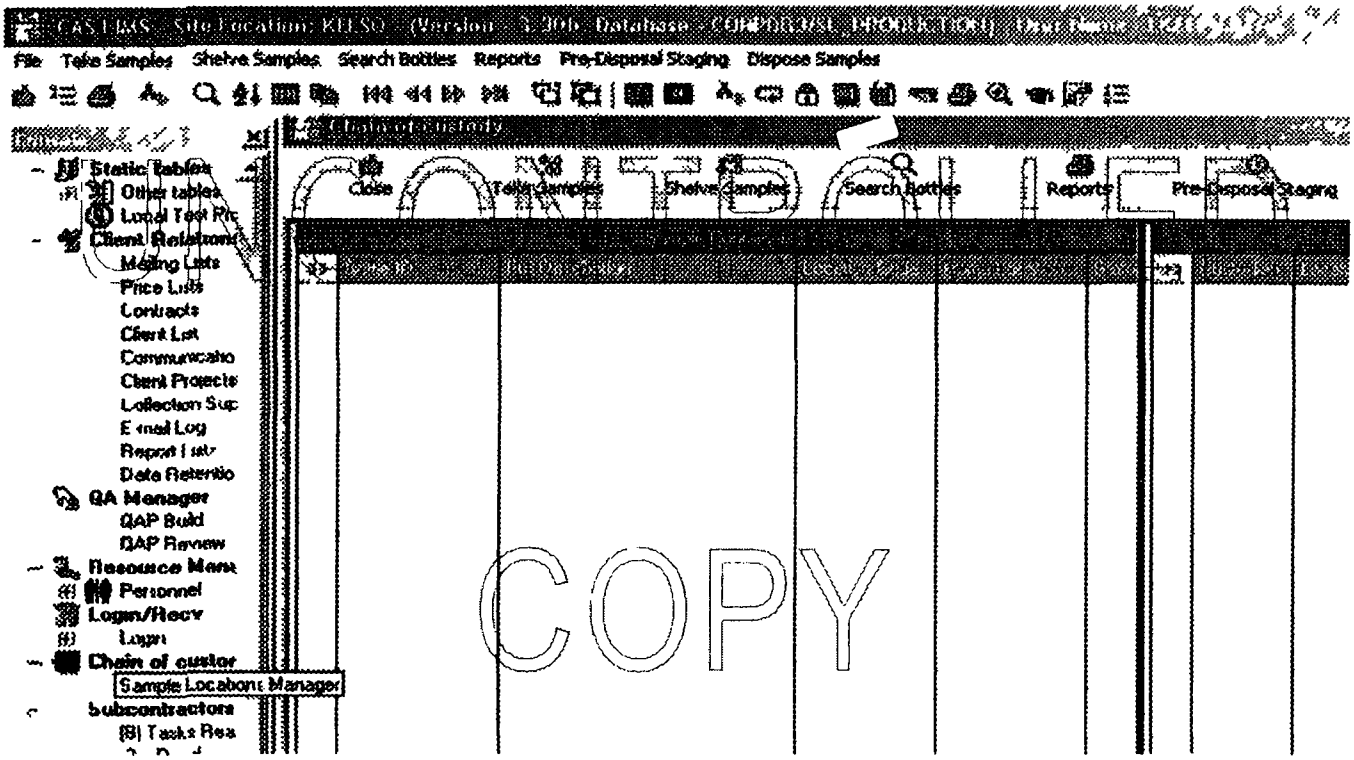
6 4 4 Using the barcode reader, read the barcode for each sample to be removed and taken into custody The sample list will appear in the window displayed It is recommended that a brief comparison of the displayed list and the actual container IDs be made

6 5 Returning samples

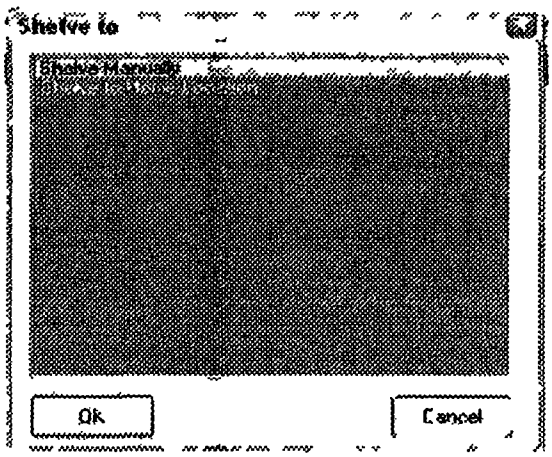
6 5 1 When the analyst is finished working with the samples the samples are returned to the main storage room and checked back in to complete the custody record If the samples are returned during business hours or when a sample custodian is on duty, the sample can be left in the designated return area and SMO will scan and shelve the samples to the home location If the samples are being returned after hours our outside the schedule of the sample custodians the analyst must scan the samples to the appropriate designation Cart in Delilah' or ' Cart in Herk etc and place the samples or sample cart in the designated refrigerator(Sec 6 5 2) SMO will retrieve and scan them to their home location and shelve them the next business day No samples other than room temperature samples can be left outside the refrigerator

NOTE Foreign soil samples or VOA samples must be scanned to their home location and placed in the proper refrigerator and shelf by the analysts or sample custodian These samples must never be placed in a refrigerator outside of the one to which they are assigned

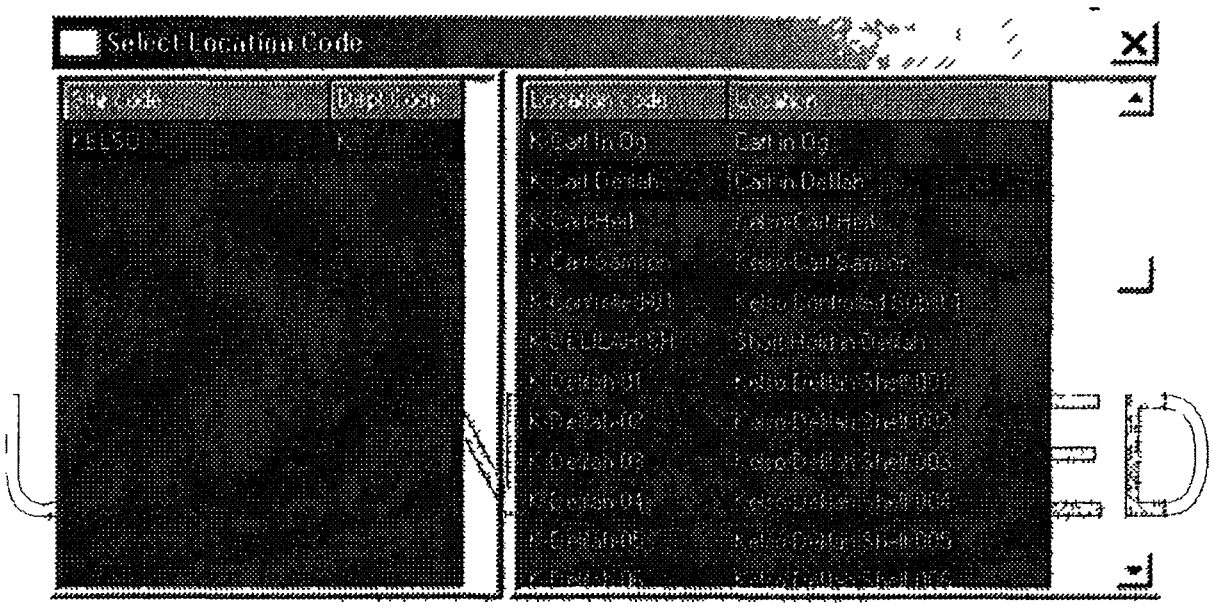
6 5 2 To return samples after hours or outside SMO hours Choose Sample Location Manager from the Chain of Custody tab and click the shelve samples button



6 5 3 Choose Shelve Manually' and click OK

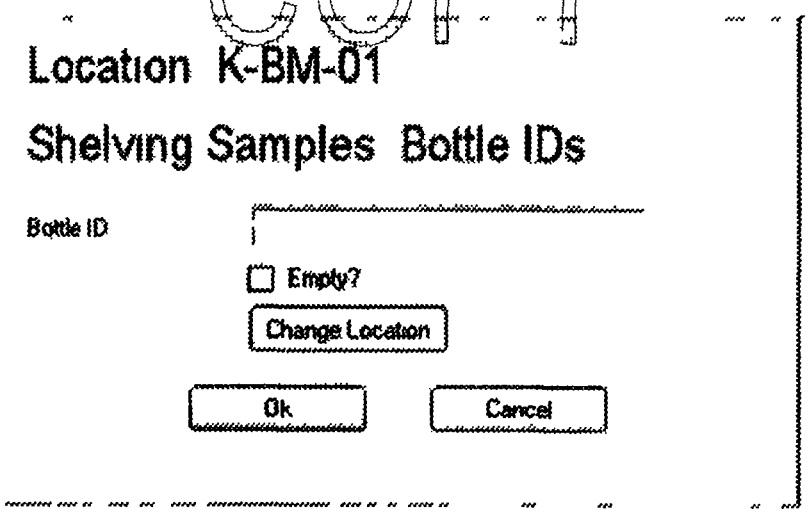


6 5 4 Choose the sample location (i e Cart in Delilah, Cart in Herk, etc) by double clicking



6 5 5 Scan each sample container DO NOT check the Empty checkbox even if the container is empty Empty containers can be left on a cart outside the refrigerator and do not need to be scanned in

COPY

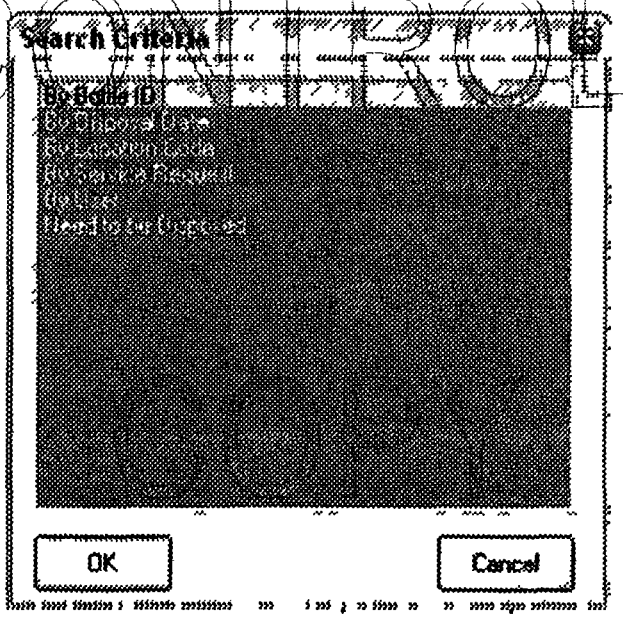


6 6 Sample tracking

6 6 1 Sample custody can be tracked via the Search function Using this function, an analyst looking for a container that is in another analyst's custody can locate the container The function is also used to document all custody events and provide internal chain of custody history At the main menu window, choose Search Bottles The Search window will appear

6 6 2 The search can be done several ways by choosing one of the criteria in the Search Criteria window The window will appear with all custody information

UNCONTROLLED



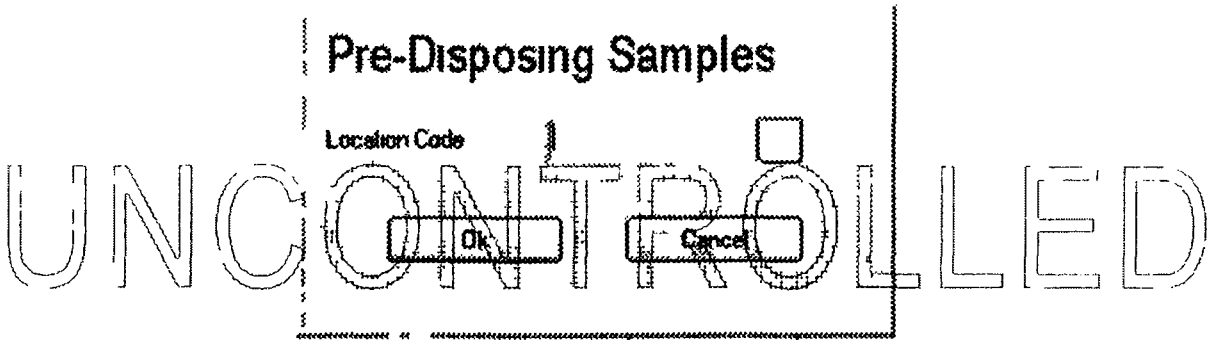
6 7 Custody of extracts and digestates

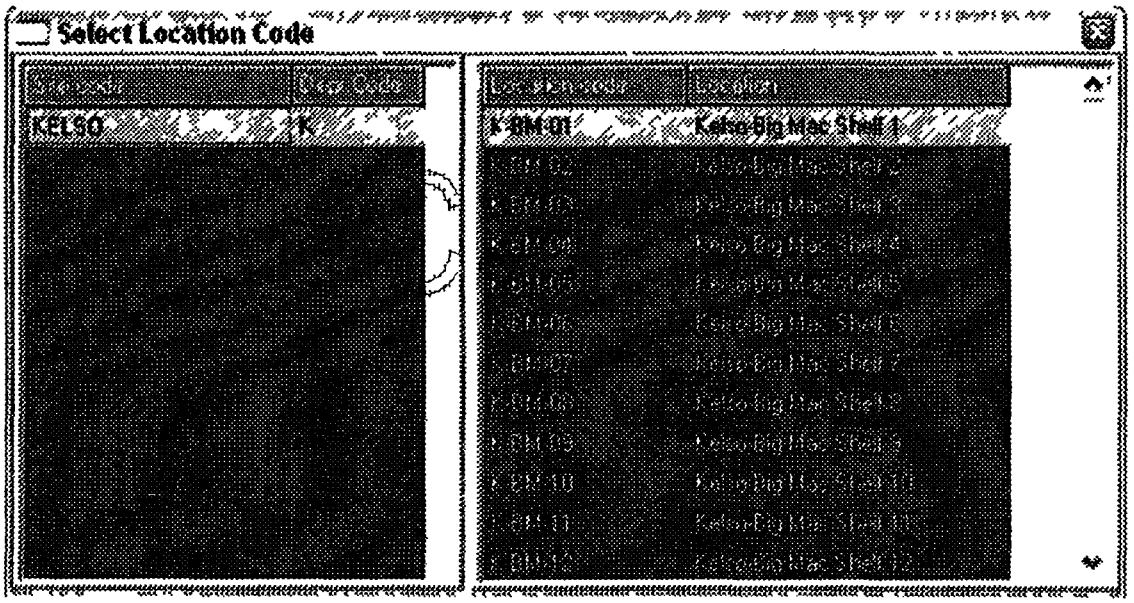
6 7 1 In labs where separate analysts prepare samples (extraction or digestion) for instrument analysis, the transfer of custody of completed extracts or digestates is documented The instrument lab analyst accepts custody of the sample extract or digestate by signing on the benchsheet, or similar custody record, that they have accepted custody of those specific extracts or digestates listed The date and time must accompany the signature

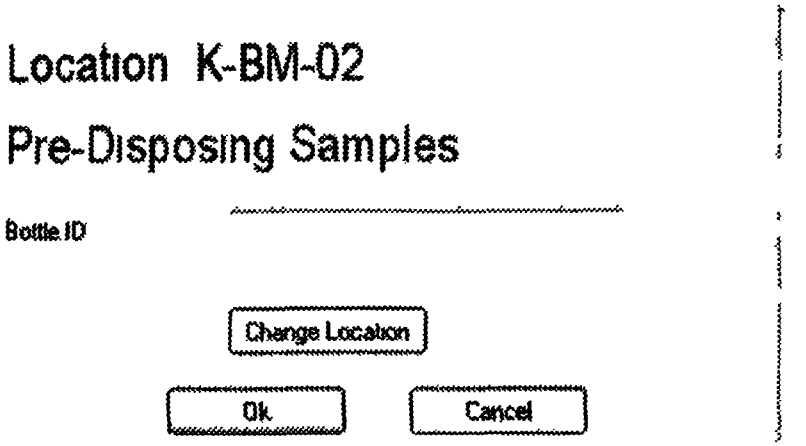
6 7 2 For TCLP extracts, the finished extracts are labeled and logged into the LIMS system as a new container for the sample The extracts are then stored as with other samples Custody and tracking is then performed as for field samples as discussed in sections 6 1 and 6 2

6 8 Pre-Disposal of Samples

6 8 1 When the analytical report has been shipped to the client, the sample containers are removed from refrigeration and placed on pre-disposal holding shelves while still in the custody of SMO The shelves are referenced in order to facilitate retrieval of a sample if necessary Transfer is documented using the Pre-Disposal and Location Selection windows

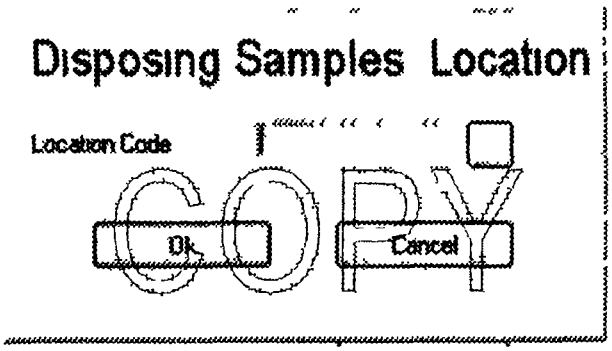




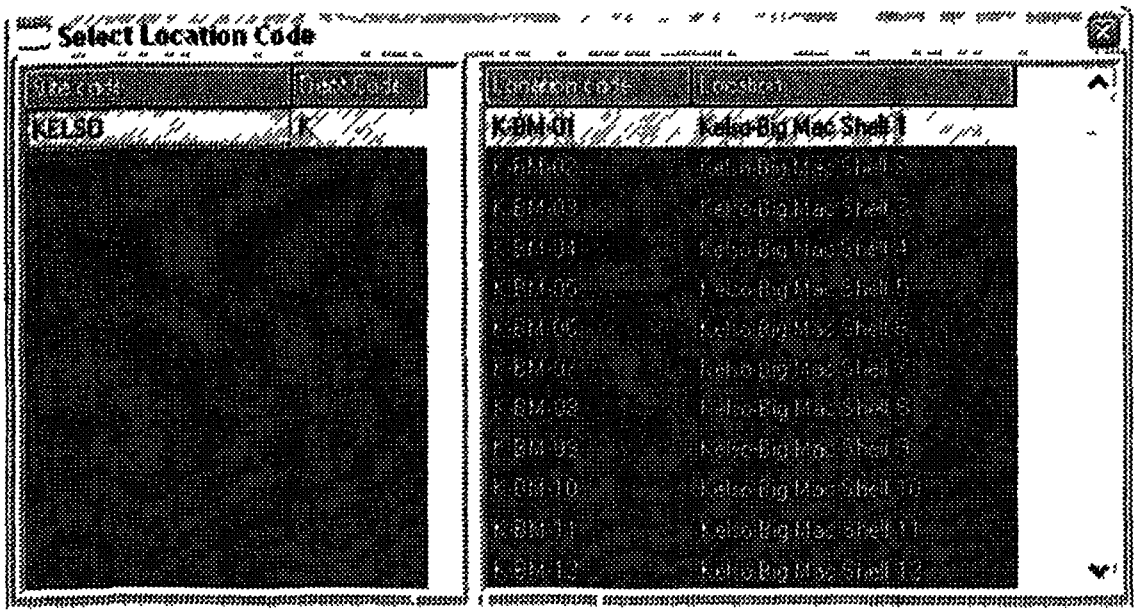


UNCONTROLLED

6.9 When sample disposal is performed, each container is scanned. Thus, the endpoint of CAS custody is documented by the final scan and documented disposal date (refer to the SOP SMO-SDIS *Sample Disposal*)



COPY

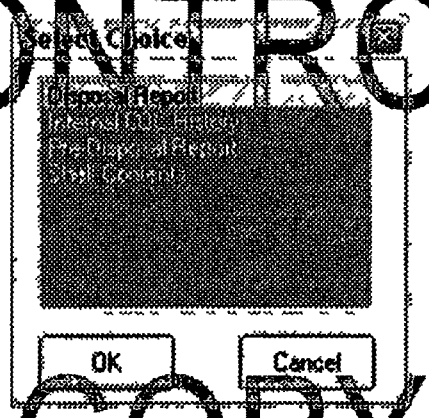


7 RECORDS AND REPORTS

7 1 Each service request will contain one or more references to the location of all of the associated sample containers The record of hazardous/non-hazardous sample determination is kept in the original service request file

7 2 After analyses are completed for the entire Service Request and the data is reported the entire sample custody record is printed and placed in the original SR file This, and other available reports, is found in the report selection window

UNCONTROLLED



COPY

7 3 Human resources and QA records are used to associate the analyst s initials to their actual handwritten signature The database of internal custody records will be maintained for 5 years Normal CAS procedures for electronic backup are used

8 CHANGES SINCE THE LAST REVISION

8 1 Sec 4 Re-wrote to make more current
8 2 Sec 5 1 Added sample custodian and analyst responsibilities
8 3 Removed old section 6 1 3 Employee unique barcode ID
8 4 Sec 6 1 1 Changed lims reference from Access to CAS LIMS
8 5 Sec 6 2 Added this section on how to request samples
8 6 Sec 6 3 How to fill a sample request
8 7 Sec 6 5 How to return samples

STANDARD OPERATING PROCEDURE

SAMPLE RECEIVING

SMO-GEN

Revision 25

April 9, 2009

UNCONTROLLED

Approved By _____ Supervisor 4/13/09 Date

_____ QA Manager 4/13/09 Date

_____ Laboratory Manager 4/13/09 Date

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2009

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

SAMPLE RECEIVING

1 PURPOSE

This procedure is used to facilitate the correct and expedient receipt login, and storage of all samples received at CAS

2 SCOPE AND APPLICATION

This procedure applies to all samples received at CAS. This procedure applies to all phases of sample handling once received, including checking and documentation of sample condition, documenting sample custody, sample login into the Laboratory Information Management System (LIMS), storage, shipping, and disposal

UNCONTROLLED

3 RESPONSIBILITIES

3 1 It is the responsibility of all lab staff who handles samples to adhere to this procedure and to complete all documentation required It is the responsibility of the department supervisor/manager to ensure that SMO staff is trained on this procedure and that training documentation is available. It is also the responsibility of the SMO supervisor to ensure that a secondary review of all sample login documentation is performed

COPY

3 2 It is the responsibility of all CAS employees to ensure the confidentiality of client information All information such as customer name and project information data, and reports is treated as confidential and is to be kept out of sight of other customers No information may be given to third parties without the consent of the client

4 DISCUSSION

4 1 The quality of analytical results is highly dependent upon the quality of the procedures used to collect and handle, and store samples Therefore sample management is a critical component of the laboratory operation This procedure ensures that samples are properly received and logged into the Laboratory Information Management System (LIMS), and that all associated documentation including chain of custody forms is complete and consistent with the samples received Complete documentation of all sample storage is maintained in order to preserve the integrity of the samples and to establish a record of sample handling All potential problems with a sample shipment are addressed by contacting the client and discussing the pertinent issues

4 2 During the log-in process each sample is given a unique laboratory code and a service request form is generated The service request contains client information sample

descriptions, sample matrix information required analyses sample collection dates analysis due dates and other pertinent information

5 PROCEDURE

5 1 Sample receipt unpacking, and inspection

5 1 1 Upon receipt sample shipping containers are examined for presence and condition of custody seals, locks, shipping bills, etc Before processing, all shipping containers (coolers) are initially opened in the hood The cooler is quickly inspected for any existing hazards such as broken bottles and a thermometer is inserted The CAS Cooler Receipt and Preservation Form (CRF – see Appendix) is used for the next steps CAS follows EPA guidelines for preservation and holding time as outlined in the CAS *Quality Assurance Manual* Table 8-1

UNCONTROLLED

NOTE If the cooler or any sample exhibits a strong odor or there is any indication of highly contaminated samples immediately transfer the cooler/samples to the hood if not already opened there Ensure that appropriate protective equipment is being used (lab coat, gloves eye protection, respirator if necessary, etc) Continue to unpack the cooler Leave the samples under the hood with the hood running Notify the Project Chemist of the sample condition For waste or product samples, store the samples in the hood in SMO For other samples (water, soil/solid, etc) store the samples in the walk-in cooler(s) If any of the suspect or highly contaminated samples are designated for VOA analysis, DO NOT store with the other VOA samples in the VOA sample refrigerator Discuss storage options with the Project Chemist and document the storage area/conditions

COPY

5 1 2 After opening shipping containers, Chain of Custody (COC) forms and any other documents are located removed, and checked for the presence of short holding time or rush samples The temperatures of the coolers are measured following the guidelines in section 5 4 of this SOP The acceptance criterion for properly chilled samples in a cooler is 4 ± 2°C If a cooler exhibits a temperature outside of the acceptance range, or exhibits any other anomalies, the CRF is attached to the Service Request and submitted for review to the appropriate project manager Samples or coolers which are received outside of the temperature range are noted on the cooler receipt form

NOTE EPA drinking water requirements for microbiology samples (surface water treatment rule and coliphage samples) require that samples be at 10°C or less If the temperature is > 10°C, the sample results must be flagged by recording the temperature in the "'Remarks" section of the Bacteriological

Analysis Form, or by noting the temperature and flagging requirement on the CRF if the results will be reported on standard forms

NOTE Some states or projects may require specific cooling requirements for shipping coolers and special cooler temperature assessment procedures For example, Wisconsin DNR does not allow the use of blue ice

5 1 3 Rush requests and samples with short holding times are given priority for initial processing For samples with extremely limited time remaining before the expiration of the holding time and that are in danger of expiring prior to being able to complete the login process, see 5 1 4 2 Sample containers are removed and organized according to chain of custody identification and analysis. Once unloaded, all SMO staff will finish the login and issuing process for short holding time and rush samples prior to working on the remaining samples Any containers that are received in broken condition or leaking are documented on the Cooler receipt Form (CRF) and on the chain of custody The appropriate Project Chemist is also notified For EPA samples which exhibit discrepancies or are damaged upon receipt, the EPA Project Chemist is responsible to notify EPA SMO for direction

UNCONTROLLED COPY

Note Samples received for NCASI Method WP-99 02 must be kept refrigerated or iced in accordance with section 6 3 of the method SOP Once the samples are identified and verified against the COC, the samples must be placed back in an iced cooler or a refrigerator until login is complete and samples can be relocated to their assigned storage location **DO NOT DELIVER SAMPLES TO THE LABORATORY**

5 1 4 Samples received with short or expiring holding times will be issued via a "Temporary Service Request" prior to the final Project Chemist review enabling the laboratory to quickly access or process the samples For samples that require wastewater microbiology testing, the analysis is to begin as soon as possible after receipt at the laboratory Holding times are assigned according to the sample type, test method and as prescribed in Standard Methods Microbiology samples received past the holding time do not meet sample acceptance requirements and a notation is made on the Bacteriological Analysis Form and/or Cooler Receipt and Preservation Form Decisions regarding the disposition of the samples that do not meet sample acceptance criteria are to be documented on the Cooler Receipt and Preservation Form by the Project Chemist

5 1 4 1 Sample receiving notifies the laboratory of short hold time samples by creating a copy of the service request for each department and stamping with "Temporary" The original service request is stamped with the "Temporary

Service Request/Custody stamp for signature of receipt by all receiving labs The appropriate bottles associated with the short hold samples are scanned to either the department (if bottles need to be delivered to the lab) or to the appropriate home location

NOTE Samples received for General chemistry with holding times expiring *before* 10am the following day are to be delivered to the laboratory for analysis All other samples (excluding VOA & foreign soils) are to be scanned to the Short Hold shelf and delivered to that location for easy retrieval by the analyst VOA and foreign soils are to be scanned to their home location and placed in the appropriate storage areas

UNCONTROLLED

5.1 4 2 If the holding time is limited and in danger of expiring prior to the completion of the login process, immediately notify the appropriate laboratory via phoning the department or via over-head paging. When notifying the department, indicate the test and the time the holding time is expiring Immediately notify the appropriate PC via phoning them or via over-head paging Complete the cooler receipt form noting any discrepancies Create two copies of the Chain of Custody and stamp one with the "Custody Transfer" stamp This copy is to remain in SMO When samples are removed from SMO the chemist signs for custody of the sample(s) noting the time taken A copy of the COC is made available to the analyst Analysts must return the original sample to SMO as soon as possible so that the login and labeling process can be completed Upon returning the sample, the analyst relinquishes custody back to SMO by signing the COC and noting the time returned SMO takes custody by signing the COC and noting the time

COPY

5 1 5 For water VOA samples (those received in 40mL VOA vials), inspect the vials for headspace

5 1 6 Listed below are items which must be verified against the chain of custody information as it applies to samples and containers received

- Sample identification
- Number of containers received
- Matrix
- Correct bottles for analysis requested
- Correct/sufficient sample volume for analysis
- Correct preservatives for analysis The CAS sample bottle preparation form is attached as a reference for proper preservatives

At this point a brief evaluation of the amount of sample provided for the requested analyses is made Compare the sample containers and estimated amount of sample provided to the analyses requested on the COC Using Table

1, determine if the amount of sample provided is at least as much as the minimum sample amount required If not, notify the Project Chemist The Project Chemist should provide further instructions for handling the sample login

5 1 7 For inorganics analyses on water samples where preservation at a prescribed pH is required check for the appropriate pH Refer to Table 2 for those analyses requiring the pH check at the time of receipt For example water samples for metals analysis require a pH of <2 and water samples for cyanide analysis require a pH of >12 The pH check is documented on the cooler receipt form which, when completed, is kept with the SDG file The pH is checked on bottles requiring certain organics analyses including oil and grease, hydrocarbon, or VOA analyses by the lab department. All pH measurements made by SMO personnel must be performed by pouring a small aliquot of sample from the bottle into a plastic weigh boat Narrow-range (increments of 0 2 units or less) pH test strips are used The pH test strips are dipped into the liquid in the weigh boat in order to measure the pH of the sample Under no circumstances is a pH test strip to be dipped directly into a sample container, due to the possibility of contamination If further preservation of the sample is needed, the appropriate acid or base is added (up to a maximum of 2mL per liter) The lot number for the preservative added is recorded on the cooler receipt and preservation form as well as the time preserved

UNCONTROLLED COPY

Note If acid is added to a metals sample at the time of login a comment is added to the Service Request indicating to the analyst that the sample was preserved at login. This indicates to the analyst that the 16-hour minimum sample holding requirement listed in the laboratory SOPs applies

5 1 8 For semivolatile organics analyses on water samples where preservation is necessary for samples with residual chlorine present, check for the presence of residual chlorine (see Table 2 for analyses required) Using a potassium iodide starch test strip pour a small amount of sample into a weigh boat and dip the strip into the weigh boat If positive the test strip will turn purple Test one bottle per sample and record the result If the test for residual chlorine is positive the sample is taken to the laboratory for addition of sodium thiosulfate solution (1mL of 10% to each applicable bottle) and documented The lot number for the preservative added is recorded on the cooler receipt and preservation form

5 1 9 Discrepancies and Broken Samples

5 1 9 1Any discrepancies or concerns from sections 5 1 1 through 5 1 6 above are noted on the COC and/or Cooler Receipt Form and communicated to the Project Chemist Any resolutions are recorded on the Chain of Custody form a nonconformity form or a phone log that is placed in the

service request master file If a Chain of Custody is not received, information is noted on a CAS Log-In Information sheet (see Appendix)

5 1 9 2 When sample identifications on bottles are different than what is on the Chain of Custody the difference is noted on the Cooler Receipt Form (CRF) and the project chemist is informed via the "Please Check" Post-it, to check the ID Once it is logged in on the service request the way the client wants and discrepancies are noted on CRF, a red check is placed on the sample bottle This informs the lab that the discrepancy has been noted If there is a discrepancy between the service request identification and the sample bottle identification and no red check is on the sample bottle, the analysts must inform SMO immediately to verify they have the right sample and it can be documented as stated above.

UNCONTROLLED

5 1 9 3 Cleanup procedures are as follows

Liquids Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box The liquid including ice, is collected and disposed of as RCRA waste Any absorbent packing material containing the liquid is collected and disposed of in the RCRA solids waste container

Soils Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box The solids are collected and disposed of in the RCRA solids waste container along with any packing material contaminated with the sample

COPY

5 1 9 4 For VOA samples in VOA vials, EPA Method 5030B states that the size of any bubble caused by degassing upon cooling should not exceed 5-6mm The presence of air bubble(s) is noted on the CRF if the bubble is $\geq$ 5mm (approximately the size of a small pea) If a bubble this size is present, the cap and septum should be inspected for breakage or leakage The Project Chemist will be notified if no other vials for the sample can be used (all vials have bubbles)

5 1 10 For EPA CLP work the following additional steps must be taken

5 1 10 1 Designated Sample Custodian

The SMO department must designate a primary sample custodian who is responsible for the log-in of EPA CLP samples An alternate representative should also be designated, the EPA PC should be aware of the identity of these people and should be notified if there is a desire to transfer this authority to a different individual

5 1 10 2Sample Log In Sheet (DC-1)

This form is used to document receipt and inspection of samples and containers A DC-1 form (see Appendix) is required for each cooler It must be completed as the cooler is opened and samples are examined as described in the applicable CLP SOW In addition to examining the items found in section 5 of this SOP, the following additional items must be reviewed and/or noted on form DC-1

- The presence/absence and condition of custody seals
- The presence/absence of chain-of-custody forms airbills or airbill stickers, traffic reports or packing lists and sample tags
- Custody seal numbers when present
- Airbill or airbill sticker numbers
- Sample tags listed/not listed on the COC records
- Date and Time of receipt
- EPA sample numbers
- Sample tag numbers

UNCONTROLLED

When the DC-1 form is completed, the sample custodian or designated alternate must provide a full signature sign-off on the report, initials are not acceptable

COPY

5 1 10 3pH Verification - Check the pH as described in section 5 1 6 Any discrepancy from this must be reported to EPA SMO

5 1 10 4Sample Traffic Reports
A traffic report is required for each Sample Delivery Group Traffic reports and an SDG cover sheet must be sent to SMO within three days of receipt of the last sample in SDG, as described in the applicable CLP SOW

5 1 10 5SDG Naming

For EPA CLP work, the following rules must be followed in forming Sample Delivery Groups (SDG) An SDG is defined by the following whichever is more frequent

- Each case of field samples or
- Each 20 field samples in a case or
- Each 14 calendar day period during which field samples in a case are received The 14-day period begins with the receipt of the first sample

The SDG number is the 6-digit EPA sample number of the first sample received in an SDG When several samples are received at the same time the lowest alpha numeric number is used CAS assigns a unique lab code to each sample The lab codes are recorded on the Chain of Custody where it is applicable

5 1 11 Samples received after normal business hours (8-5 Monday – Friday and 8-12 on Saturday) are stored in a cooler in an appropriate refrigerator and are fully processed the following day Upon receipt, an After Hours Receipt Form is completed and the temperature of the cooler is recorded in accordance with section 5 4 of this SOP (Note the temperature must be recorded from the temperature blank if one is present) If samples are received the same day they are collected they can be placed in appropriate cold storage without determining cooler temperatures (In this case, samples are considered acceptable if there is evidence that the chilling process has begun and they do not need to meet the criteria of being within 2° C of the required temperature) The location of storage is noted on the After Hours Receipt Form (i e Samson, Herk, etc)

UNCONTROLLED

5 1 12 The chain of custody form will be signed when the log-in procedure is completed (on the next working day if the samples are received after hours)

5 1 13 Courier Service

COPY

CAS provides a Courier Service for our Clients from our Kelso Laboratory Southbound to the Portland Metropolitan area to pick up samples When picking up samples from Clients, a Courier/After-Hours Sample Receipt Record is filled out and signed by our Courier and also by the Client/Sampler Information such as date & time of pick-up, the Company name, number of containers, project number and if custody seals were present or added are noted on this Receipt Form The Courier retains a copy of the Courier/After-Hours Sample Receipt Record and this copy is placed in the Master File once the job is logged into the LIMS system in the laboratory The original copy is given to the Client at the time the CAS Courier takes possession of the samples

5 2 Sample Login

5 2 1 Each job received at the laboratory is logged into the Laboratory Information Management System (LIMS) Access to LIMS Login is limited to Sample Management Staff and Project Chemists The LIMS will assign the next available Service Request number The Service Request number is made up to identify the CAS lab the year and then a numeric number (i e K0502250 K for the Kelso lab 05 for the year and then 02250 would be the next number available in the system)

5 2 2 The client and project are identified in the LIMS based on the COC information The Sample Delivery Group (SDG) sample template is chosen and transferred to the login If needed the requested tests are added The sample identifications date and time of collection and date received are entered The date on which the laboratory takes possession of the samples is defined as the date the COC is signed For after-hours sample receipt where the after hours receipt form is used, the COC is not signed until the next business day (see 5 1 11) If the collection time is not provided a conservative estimate of the time is made In cases where the client and project information is not in LIMS the PC is contacted to setup the project or give instruction to the SMO staff as to how to set up the project

UNCONTROLLED

5 2 3 Each test is automatically assigned a container ID in LIMS The specific containers received are reconciled at the time of login

5 2 4 The service request report is printed and a master Service Request File is created Another person in the Sample Management group performs a login review The master SR file is then given to the Project Chemist for final review before being issued to the laboratories The Project Chemist reviews the service request form before being issued to the analysts For analyses with short holding times (generally 48 hours and less) other samples near holding time expiration, and RUSH samples (due within 5 days), a "Temporary Service Request" is issued directly to the applicable department, whose representative signs off on receipt of the service request SMO also prints a "2-day report" from LIMS that identifies all analyses with holding times expiring within 2 days and due dates within 2 days

COPY

5 2 5 Lab Codes and Sample Identification/Labeling

Each sample is given a unique sample lab code by the LIMS system This number is designated by the service request number, followed by a dash, a sequential number, a period and a container ID (e g K0504567-001 01), where K0504567 represents the service request number, -001 represents the sample and 001 represents the container Thus, each sample is given a unique ID Samples are reviewed to make sure the lab codes match the correct sample identification on the service request and that correct bottles were received for the analyses

5 2 6 Solid Samples Labeling

5 2 6 1If the quantity of sample given to the laboratory is insufficient for the analyses requested, the sample container should be labeled with Limited Sample Quantity (or something similar) or attach a "LIMITED SAMPLE VOLUME" tag The project chemist will set the priorities for the analyses and if possible estimate the quantity of sample to be used for

each test This information should be documented and communicated to the lab via a Form V For example, 8081 use 10 g metals use 1 g, TCLP use 20 g

NOTE Samples that are quantity limited and require multiple analyses from a single container must be identified as soon as possible Optimally, this should happen during sample login, however, discovery at any time should follow the same process When it is discovered that a sample is quantity limited, the quantity of wet sample available is estimated and the project chemist is immediately notified The project chemist should attempt to prioritize the tests most critical to the client (*i e* which test should be performed first) and estimate the sample quantity allotted to each test

UNCONTROLLED

5 2.6 2Solid Samples Requiring VOC and Non-VOC Analyses with One Container

When only one container is received and both VOC and non-VOC analyses are requested, SMO will attach a "VOA FIRST" tag to the jar and indicate the tests required

The VOC department will remove a sample aliquot first for the VOC analyses. The VOC department will handle the sample as if it were a Rush analysis, so that the other non-VOC analyses will not be unduly delayed The VOC chemist who opens the container will initial and date the "VOA FIRST" tag next to the appropriate test A ***VOC Analysis First*** note will also be included on the SR

COPY

Sample aliquots for non-VOC analyses may not be taken from the sample container until the aliquot for the VOC analyses has been removed Once the aliquot for the VOC analyses has been taken from the sample container, sample aliquots for the non-VOC analyses can be removed as prescribed in the various applicable analytical SOPs

5 2 6 3For solid samples requiring VOC and Non-VOC analyses with multiple containers, one of the sample containers will be designated for VOC analyses by either placing a custody seal or a "VOA FIRST" tag on the container

5 3 Login Review

5 3 1 A peer review of the login and newly generated Service Request (SR) is done by the SMO staff The SR is compared to the chain-of-custody to ensure that correct and complete information is entered on the SR Refer to the SMO Login Review sheet (see Appendix)

In some cases (i e more complex projects) and at the Project Chemist s discretion, the SMO peer review may be performed by the Project Chemist In this case the review of the folder is documented by the Project Chemist when updating LIMS and/or initialing the service request

5 3 2 As mentioned in section 5 2 3 above, the Project Chemist performs a final review of the login At a minimum this must include a close examination of the SR and chain-of-custody to verify that the SR generated by SMO accurately reflects the specifications for the project and samples The Project Chemist may also need to refer to other project-related information such as project QAPPs, client communication records, etc If the SR does not accurately specify the work requirements, is incorrect, or is incomplete, the Project Chemist makes the needed changes and the draft SR file returned to SMO for revision Once the SR is correct, the Project Chemist documents the review by signing the original SR

UNCONTROLLED COPY

5 4 Thermometer calibration and temperature measurement

5 4 1 The QA department performs thermometer calibration on all thermometers used to monitor sample storage temperature (see SOP ADM-SEMC) Each storage thermometer is given a unique numerical identification tag if one does not already exist, and all records of calibration are kept in the thermometer calibration notebook The correction factor is recorded on the thermometer label

5 4 2 Temperature measurement is performed for coolers using calibrated digital thermometers The thermometer is plunged into the packing material, if possible, or placed as deep into the cooler as is practical and the lid closed When coolers are packed such that samples are isolated from the main cooler compartment via plastic bag and/or insulation (foam vermiculite, etc), place the thermometer down into the sample area When multiple samples are in one large bag, place the thermometer in the bag Do not just place thermometer on top of the bag or insulating material The equilibration time is a minimum of 10 minutes

5 4 3 The correction factor is applied to the temperature given by the thermometer after a measurement, and it is the corrected temperature that is recorded on the CRF As an example, if the correction factor is -0 5, and the thermometer reads 5 9°C then the corrected temperature is 5 4°C If a temperature blank is present the same thermometer is used to read the temperature blank when the cooler is unpacked After measurement of the temperatures all of the information is recorded in the appropriate space on the cooler receipt form

Note A temperature blank is generally considered more indicative of sample temperature inside the cooler Where a temperature blank is present its temperature reading is considered the *primary* temperature of the cooler and the

second reading obtained from the thermometer placed in the cooler is for additional information

5 5 Sample Storage, Security, and Internal COC

5 5 1 There are a number of refrigerators, freezers, and room temperature storage areas dedicated to specific storage requirements (e g Water VOCs, Soil VOCs, etc) All of the sample storage facilities are located in the secured area Samples are held in refrigerators until analysis is completed and reported to the client Refrigeration of all non-tissue samples is maintained at a temperature of 4 ± 2° C unless otherwise specified by the state project, or client specific protocols Exception: Soil and sediment sample for designated for mercury analysis by EPA Method 1631 are stored frozen upon receipt. Tissue samples are stored in freezers at -16 to -24° C Room temperature sample storage is specified in some cases

UNCONTROLLED

Note If a new or moved storage unit is to be placed in service QA must be notified before using it so it can be monitored for acceptable conditions QA will document and approve the unit for use prior to using for sample storage Once SMO is notified, QA will begin regular monitoring

5 5 2 When samples are labeled accordingly with lab codes they are placed in appropriate refrigerators in a secured area. This area is secured with combination locks which can be accessed by technical laboratory personnel, project managers, administrative support personnel and all senior staff members Location of samples is recorded on the Service Request form and in internal COC records

COPY

5 5 3 Internal COC procedures for checking samples in and out are described in the SOP SMO-SCOC *Sample Tracking and Laboratory Chain of Custody* The SMO department has a Sample Custodian who is responsible for retrieving/returning samples from/to storage for analysts The Sample Custodian checks the samples back into custody/storage See the SOP SMO-SCOC for specific guidance

5 5 4 As an alternative to the Sample Custodian sample retrieval system analysts may retrieve and check samples out/in directly themselves

NOTE Regardless of which procedure is used, the analyst is responsible for taking custody of the sample in LIMS, ensuring the internal chain of custody of samples is accurately documented It is also the responsibility of the analyst to return samples to the storage area when work is completed, and relinquishing custody in LIMS

5 5 5 When a soil or sediment sample jar is broken during sample storage a determination has to be made whether or not the sample is salvageable (i e whether or not the sample has been completely compromised) If there is any question in determining whether a sample is completely compromised contact the PC If a tissue sample is broken during storage immediately contact the PC for direction

5 5 5 1 If some or the entire sample is salvageable scan the broken bottle as "broken" in LIMS Transfer the sample to a new container (if unsure of the transfer process or there are concerns with contamination contact the PC or appropriate laboratory department supervisor) and assign a new container ID to the sample in LIMS Label the new container with a barcode label.

UNCONTROLLED

5.5 5.2 If the sample is not salvageable notify the PC and determine if there is additional sample available for analysis Scan the broken bottle as "broken" in LIMS and dispose of the sample in the appropriate waste stream (if hazards cannot be determined at the time the sample is lost place it in a ziplock baggie, label it, and place it on pre-disposal shelf for later determination)

5 5 6 Once the Analytical Report has been mailed to the client, the Internal Chain of Custody record from the bar-coding system database is printed and retained in the Service Request File

COPY

5 6 Sample Disposal

After all analyses have been completed and the Certified Analytical Report (CAR) has been generated and mailed to the client the associated samples are pulled from refrigeration and stored on shelves located in the secure storeroom area An assessment is made of the nature of the samples (i e hazardous or non-hazardous) and the samples disposed of accordingly Water samples are held for 31 days and soil samples for 2 months unless contractual obligations supersede these parameters Fish and invertebrate animal tissue samples are held at -20°C for 90 days after reporting After the holding period has expired, samples are disposed of using appropriate disposal procedures provided by the health and safety officer and/or committee This task is performed by qualified SMO personnel

5 7 Sample Shipping to Outside Labs

5 7 1 The sample is logged in and the specific product code or "misc outside" is used for subcontracted analysis A list of routinely subcontracted analyses is attached

5 7 2 For CAS Network Labs using LIMS the samples are shipped with a chain of custody indicating the analyses to be performed

5 7 3 For other labs a purchase order (if non CAS lab) and chain of custody is filled out for work going to another subcontract laboratory TAT, deliverables,etc are specified Prior to shipment SMO personnel perform a review of the COC against samples subcontracted Samples to be shipped to an outside lab are stored in a refrigerator near SMO

5 7 4 A shipping form is completed by SMO and given to the shipping department for shipment

5 7 5 Samples are prepared for shipping by the shipping department by packing in the appropriate packing material, placing blue ice, samples, and the chain of custody in shipping coolers Custody seals are signed and dated and placed on the front and/or side of the cooler The cooler is then sealed with packaging tape A "Sample" label is placed on the cooler

UNCONTROLLED

5 7 6 Samples that are relinquished to another laboratory that reports all of their data directly to the client and bills the client directly do not need to be logged in

6 RECORDS

All sample receipt records, including COC forms CRFs, Service Requests, sample information, etc is filed in the master service request file

COPY

7 CHANGES IN SOP SINCE THE LAST REVISION

7 1 Sec 5 1 2 Added statement to check for sort holds time or rush samples
7 2 Sec 5 1 2 Removed statement - For WDNR, it should be noted if regular ice was present in the cooler
7 3 Sec 5 1 3 added language to clarify how to handle short HT samples
7 4 Sec 5 1 4 1 Added language to clarify how to handle short HT samples
7 5 Sec 5 1 4 2 Added language to clarify how to handle short HT samples
7 6 Sec 5 1 7 Added requirement to record the time preserved
7 7 Sec 5 1 9 7 Removed sentence - For method 1631 samples, inspects the sample for the presence of headspace Document on the CRF if present
7 8 Sec 5 5 3 Referenced SMO-SCOC SOP
7 9 Sec 5 5 5 Added procedure to follow when container is broken in the lab
7 10 Sec 5 4 1 Corrected SOP name

Table 1

Minimum Sample Volume Requirements

Measurement	Matrix	
Inorganics	**Water (ml)**	**Soil (g)**
Color	50	--
Conductance	100	10
Hardness	100	-
pH	50	50
TSS	200	--
TDS	100	--
TS	100	10
TVS	100	10
Settleable Solids	1000	-
Turbidity	100	--
Total Metals	100	10
Metals w/reductive ppt	1000	-
Dissolved Metals	100	-
Acidity	100	--
Alkalinity	100	--
Bromide	50	10
Chloride	50	10
Cyanide	500	10
Fluoride	50	10
Ammonia as N	50	10
TKN	500	10
Nitrate+Nitrite	100	10
Nitrate	50	10
Nitrite	50	10
Orthophosphorus	100	10
Total Phosphate	100	10
Sulfate	50	10
Sulfide	500	25
Sulfite	500	--
BOD	1000	50
COD	50	25
TOC	50	25
Total Phenols	500	25
MBAS	500	--
AOX/TOX	500	

UNCONTROLLED COPY

Table 1

Minimum Sample Volume Requirements (continued)

Measurement	Matrix	
Organics	**Water (ml)**	**Soil (g)**
Oil and Grease	1000	25
DRO	500	30
Pesticides (8081A,8141)	1000	30
PCP (8151M)	40	30
PCBs (8082)	1000	30
PAHs (8270C, 8310)	1000	30
Semivolatiles (8270)	1000	30
GRO	2-40ml vials	30
BTEX (8021B)	2-40ml vials	30
Volatiles (8260B)	2-40ml vials	30
Dioxins	1000	30

UNCONTROLLED COPY

Table 2

Sample Preservation Requirements

Inorganics pH Requirements

Analysis	Preservation requirement (pH)
Metals (total) except CrVI and Hg	<2
TOC	<2
COD	<2
Ammonia	<2
TKN	<2
Total Phosphorus	<2
Nitrate/Nitrite	<2
Sulfide	>9
Cyanide	>12
TOX/AOX	<2

UNCONTROLLED COPY

Semivolatile Organics Residual Chlorine Requirements

Analysis	Requirement
Semivolatile Organics (625 and 8270)	None present
Organochlorine Pesticides (608 and 8081)	None present
Herbicides (8151)	None present

Appendix

Cooler Receipt and Preservation Form
Login Information Sheet
DC-1 Form
SMO Login Review Form
Procedure for Salvaging Broken Samples

UNCONTROLLED

COPY

K09_____

Initial Login Review ☐ Revision Review ☐

Check the following information before the sample containers are shelved

	Y	N	Is the CRF completed? (resolutions noted etc)
	Y	N	Are all bottles correctly labeled? (Client name vs Lab code & number)
	Y	N	Is the Matrix consistent with the Chain of Custody (COC) and the bottles?
	Y	N	Are bottles labeled with the correct shelf number?
NA	Y	N	If indicated on the COC are samples designated for QC specified on the SR?

Reviewed By _____ Date _____

Check the following information on the service request against the information on the COC:

UNCONTROLLED

NA	Y	N	Are sample names spelled correctly on the service request (SR)?
NA	Y	N	Is the date collected for each sample correct on the SR?
NA	Y	N	Is the date received correct on the SR? Multiple dates received?
NA	Y	N	Is the project name correct (as listed on the COC)? Discrepancies noted?
NA	Y	N	Is the project number correct (as listed on the COC)? Discrepancies noted?
NA	Y	N	Is the Tier level correct (as listed on the COC)? Discrepancies noted?
NA	Y	N	If listed on the COC is the PO Number correct on the SR?
NA	Y	N	Are all the samples indicated on the COC logged in?
NA	Y	N	Are all analyses indicated on the COC logged in?
NA	Y	N	For RUSH TAT does the due date listed on the SR make sense? Is the Rush flag flipped?
NA	Y	N	If any are the pertinent comments on the COC indicated on the SR? (i e metals lists volume limitations hazards etc)
NA	Y	N	Has a temporary SR been issued for short hold times and/or 24-48hr rushes?
NA	Y	N	If preservative was added upon receipt is it indicated on the SR?
NA	Y	N	Does the SR contain appropriate additional product codes such as EDD DOD Sample Prep Filter codes TS Met?
NA	Y	N	Is the two Day report printed?
NA	Y	N	If needed is the Sub Chain printed for outside shipping?
NA	Y	N	Is the COC signed by SMO?

COPY

Reviewed By _____ Date _____

Cooler Receipt and Preservation Form

Client / Project _____ Service Request *K09* _____

Received _____ Opened _____ By _____

1 Samples were received via? *US Mail* *Fed Ex* *UPS* *DHL* *GH* *GS* *PDX* *Courier* *Hand Delivered*

Samples were received in (circle) *Cooler* *Box* *Envelope* *Other* _____ *NA*

3 Were custody seals on coolers? NA Y N If yes how many and where? _____

If present, were custody seals intact? Y N If present, were they signed and dated? Y N

Is shipper s air bill filed? If not record air bill number _____ NA Y N

Temperature of cooler(s) upon receipt (°C)			
Temperature Blank (°C)			
Thermometer ID			
If applicable list Chain of Custody Numbers			

7 Packing material used *Inserts* *Baggies* *Bubble Wrap* *Gel Packs* *Wet Ice* *Sleeves* *Other* _____

Were custody papers properly filled out (ink signed, etc)? NA Y N

9 **Did all bottles arrive in good condition (unbroken)?** *Indicate in the table below* NA Y N

10 Were all sample labels complete (i e analysis preservation etc)? NA Y N

11 Did all sample labels and tags agree with custody papers? *Indicate in the table below* NA Y N

12 **Were appropriate bottles/containers and volumes received for the tests indicated?** NA Y N

13 Were the pH preserved bottles tested* received at the appropriate pH? *Indicate in the table below* NA Y N

14 Were VOA vials received without headspace? *Indicate in the table below* NA Y N

15 **Are CWA Microbiology samples received with >1/2 the 24hr hold time remaining from collection?** NA Y N

16 Was C12/Res negative? NA Y N

UNCONTROLLED

COPY

Sample ID on Bottle	Sample ID on COC	Sample ID on Bottle	Sample ID on COC

Sample ID	Bottle Count Bottle Type	Out of Temp	Head-space	Broke	pH	Reagent	Volume added	Reagent Lot Number	Initials	Time

oes not include all pH preserved sample aliquots received See sample receiving SOP (SMO GEN)

Additional Notes, Discrepancies, & Resolutions _____

Columbia Analytical Services Inc
Cooler Receipt and Preservation Form

Client / Project _____ Service Request *K09* _____

Sample ID on Bottle	Sample ID on COC	Sample ID on Bottle	Sample ID on COC

Sample ID	Bottle Count Bottle Type	Out of Temp	Head space	Broke	pH	Reagent	Volume added	Reagent Lot Number	Initials	Time

UNCONTROLLED COPY

Additional Notes, Discrepancies & Resolutions _____

STANDARD OPERATING PROCEDURE

for

MERCURY IN WATER BY OXIDATION, PURGE AND TRAP, AND COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY

SOP No MET-1631

Revision 9

March 21, 2008

UNCONTROLLED

Approved by _____ Supervisor _____ Date

_____ QA Manager _____ Date 3-21-08

_____ Laboratory Manager _____ Date 3/27/08

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2008

Annual review of this SOP has been performed and the SOP still reflects current practice	
Initials JDB	Date 3/13/09
Initials _____	Date _____
Initials _____	Date _____

DOCUMENT CONTROL	
NUMBER _____	
Initials _____	Date _____

MERCURY IN WATER BY OXIDATION, PURGE AND TRAP, AND COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY

1 SCOPE AND APPLICATION

1 1 This procedure is used to determine the concentration of Mercury in aqueous samples including wastewater, aqueous wastes and ground water, using EPA Method 1631E

1 2 Method 1631 is a cold vapor atomic fluorescence procedure used in determining the total mercury (Hg) in filtered and unfiltered water samples This method is designed for the measurement of total Hg in the range of 0 2 - 100 ng/L With use of an additional calibration standard the range may be extended to 200 ng/L if necessary.

UNCONTROLLED

1 3 Total mercury as defined by this method means all BrCl-oxidizable mercury forms and species found in aqueous solution This includes but is not limited to Hg(II), Hg(0) strongly organocomplexed Hg(II) compounds adsorbed particulate Hg and several covalently bound organomercurials (i e CH_3HgCl, $(CH_3)_2Hg$ and $C_6H_5HgOOCCH_3$) The recovery of Hg bound within microbial cells may require the addition step of UV photo-oxidation

2 METHOD SUMMARY

COPY

Samples are collected in new 500 mL Fluorinated LPE bottles The samples are preserved with 1 1 HCl in the field, and with a BrCl solution at the lab Samples are prepared for analysis by the addition of 5ml/L of BrCl solution or aliquoting 100 mL into pre-cleaned HDPE digestion vessels and oxidizing with BrCl solution After oxidation the samples are pre-reduced with NH_2OH HCl to destroy free halogens, and then reduced with $SnCl_2$ to convert Hg(II) to volatile Hg(0) Solid samples are prepared by HNO_3/ H_2SO_4 digestion than diluted with dilute BrCl solution to 40mls An aliquot of 5ml is added to 100mls of prepurge water The Hg(0) is separated from solution by purging with argon onto a gold trap The trapped Hg is then thermally desorbed from the gold trap into an Ar gas stream that carries the Hg into the cell of the Brook Rand Model III cold-vapor atomic fluorescence spectrometer (CVAFS) for detection

3 DEFINITIONS

3 1 **Analysis Sequence** - Samples are analyzed in a set referred to as an analysis sequence The sequence begins with instrument calibration followed by sample analyses interspersed with calibration standards

3 2 **Quality Control Sample (QCS)** - QCS solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization

3 3 **Matrix Spike** (MS) - In the matrix spike analysis predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to sample preparation and analysis The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses Percent recoveries are calculated for each of the analytes detected

3 4 **Matrix Spike Duplicate** (MSD) - In the matrix spike duplicate analysis predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to sample preparation and analysis The purpose of the matrix spike duplicate is to evaluate the effects of the sample matrix on the methods used for the analyses Percent recoveries are calculated for each of the analytes detected The relative percent difference between the matrix spikes is calculated and used to assess analytical precision

UNCONTROLLED

3 5 **Duplicate Sample** (DUP) - A laboratory duplicate The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper The relative percent difference between the samples is calculated and used to assess analytical precision

3 6 **Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process The method blank is carried through the entire analytical procedure In addition to method blanks, additional blanks are described within the procedure

3 7 **Ongoing Precision Recovery (OPR)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration

COPY

3 8 **Calibration Verification (VER)** – is spiked reagent water sample (aqueous blank spike) and is used to determine that the CVAFS remains in control

4 INTERFERENCES

4 1 It is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace mercury Potential sources of contamination during sampling include metallic or metal-containing labware containers, sampling equipment, reagents, and reagent water improperly cleaned and stored equipment, labware, and reagents, and atmospheric inputs such as dirt and dust Even human contact can be a source of trace mercury contamination (e g mercury fillings)

4 2 Within the laboratory, interferences from contaminated reagents must be minimized Ultrex acids and reagent grade chemicals are used to prepare the reagents To minimize contamination all sample preparation should be performed in the Class 100 clean hood Before a given batch of samples is processed all work surfaces in the hood or clean bench where the samples will be processed should be cleaned by wiping with a lint free cloth or wipe soaked with reagent water

4 3 All apparatus used for determination of mercury at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both

4 4 Samples are taken in fluorinated LPE containers These containers have a thin coating of a fluoropolymer

4 5 It may be useful to dedicate separate sets of labware to different sample types e g, receiving waters vs effluents However, the apparatus used for processing blanks and standards must be mixed with the apparatus used to process samples so that any contribution of contamination from all labware can be randomly assessed

4 6 Water vapor may collect in the gold trap and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of excitation radiation Condensation can be avoided by predrying the gold trap, and by discarding those traps that tend to absorb large quantities of water vapor

UNCONTROLLED COPY

4 7 Bottle blanks--After undergoing the cleaning procedures in this method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures A representative set of sample bottles should be filled with reagent water acidified to pH < 2 and allowed to stand for a minimum of 24 hr After standing, the water should be analyzed for any signs of contamination If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles re-cleaned This is done through the preparation of method blanks weekly

5 SAFETY

5 1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment, such as safety glasses, lab coat and the correct gloves

5 2 Chemicals, reagents and standards must be handled as described in the CAS safety policies approved methods and in MSDSs where available Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method

5 3 Hydrochloric and/or Nitric Acid are used in this method These acids are extremely corrosive and care must be taken while handling them A face shield should be used while pouring acids And safety glasses should be worn while working with the solutions Lab coat and gloves should always be worn while working with these solutions

5 4 Chronic mercury exposure may cause kidney damage muscle tremors spasms personality changes, depression, irritability and nervousness Organomercurials may cause permanent brain damage Because of the toxicological and physical properties of the Hg, pure

standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks

5 5 CAS purchases a dilute standard solution of Hg for this method If primary solutions are prepared, they must be prepared in a hood

5 6 Hands should be washed thoroughly after each manipulation and before breaks

5 7 The cleanliness of work surfaces and tools may be assessed by wiping the surface with a piece of filter paper Extraction and analysis by this method can achieve a limit of detection of less than 1 ng per wipe Less than 0 1 mg per wipe indicates acceptable cleanliness, anything higher warrants further cleaning More than 10 mg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed

UNCONTROLLED

6 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6 1 CAS laboratory staff does not collect samples Samples are collected by field sampling staff of CAS customers using their sampling plans and procedures In some cases persons collecting samples may be required to be certified by regulatory bodies Samples are either field- or laboratory-preserved by adding 5 mL of 6N (1 1) HCl to a 500 mL Fluorinated LPE bottle Upon receipt at the laboratory samples are taken to the clean room and BrCl (2 5ml/500ml) is added

COPY

6 2 Samples that are acid-preserved only may lose Hg to coagulated organic materials in the water or the Hg may be condensed on the walls (Reference 19 11) The bottle should be vigorously shaken before sub-sampling to re-suspend the organic matter

6 3 All handling of the samples in the laboratory should be undertaken in a mercury-free clean bench

6 4 Water samples are typically stored at 4 ± 2°C until analysis However, this is not a method requirement and samples may be stored at room temperature if necessary The maximum holding time for mercury in unpreserved aqueous samples is 48 hrs Once preserved, aqueous samples have maximum holding time of 90 days Solid samples have a holding time of 1 year if stored in a freezer at < -15°C Samples that are freeze dried have a holding time of 1 year, also

6 5 Field blanks – Field blanks are used to demonstrate that samples have not been contaminated by the sample collection and transport activities

6 5 1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time to a maximum of 10 samples) Analyze the blank immediately before analyzing the samples in the batch

6 5 2 If Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes

6 5 3 Alternatively, if sufficient multiple field blanks (a minimum of three) are collected, and the average concentration (of the multiple field blanks) plus two standard deviations is equal to or greater than the regulatory compliance limit or equal to or greater than one-half of the level in the associated sample results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes

UNCONTROLLED

6 5 4 If contamination of the field blanks and associated samples is known or suspected the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event

6 6 Equipment blanks—Before any sampling equipment is used at a given site equipment blanks (bottle blanks and sampler check blanks) must be submitted to the laboratory to demonstrate that the sampling equipment is free from contamination Sampler check blanks are generated by processing reagent water through the sampling devices using the same procedures that are used in the field Refer to Method 1631E for details

COPY

7 APPARATUS AND EQUIPMENT

7 1 Cold vapor atomic fluorescence spectrometer (CVAFS) Brooks-Rand (Seattle WA) Model III CVAFS or equivalent

7 2 Flowmeter, with needle valve capable of reproducibly keeping the carrier gas flow rate at 60 mL/min

7 3 Pyrex bubbler with 4 way Teflon stopcock, 220 mL (Brooks-Rand Seattle WA, part no AF-32 or equivalent)

7 4 Flow meter/needle valve capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min

7 5 Fluoropolymer fittings Connections between components and columns are made using 6 4-mm o d fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing

connectors Connections between components requiring mobility are made with 3 2-mm o d fluoropolymer tubing because of its greater flexibility

7 6 Acid fume pre-trap 10-cm long x 0 9-cm i d fluoropolymer tube containing 2-3 g of reagent grade, non-indicating ~14 mesh soda lime chunks, packed between wads of silanized glass wool This trap must be cleaned of Hg by placing on the output of a bubbler containing reagent water and $SnCl_2$ and purging for 45 minutes with Ar

7 7 Gold-coated sand trap or gold wire trap 10-cm x 6 5-mm o d x 4-mm i d quartz tubing The tube is filled with 3 4 cm of gold-coated 45/60 mesh quartz sand (Brooks Rand, Ltd Seattle, WA, Part No AF-20 or equivalent) The ends are plugged with quartz wool A gold wire trap is also available from Brooks Rand (Part No AF-19)

UNCONTROLLED

7 8 Traps are fitted with 6 5-mm i d fluoropolymer friction-fit sleeves for making connection to the system When traps are not in use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination At least 16 traps are needed for efficient operation

7 9 Heating of gold-coated sand traps To desorb Hg collected on the traps heat for 2-3 minutes to 450-500°C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 10 Vac Potential is applied and finely adjusted with a variable transformer

7 10 Air blower After heating, the trap is cooled by blowing air from a small blower positioned immediately below the trap

COPY

7 11 Computer (386 or better) and Windows Mercury Guru software to record and integrate the signal from the spectrometer

7 12 Pipettors All-plastic pneumatic fixed-volume and variable pipettors in the range of 20 uL to 1 0 mL

7 13 Analytical balance capable of weighing to the nearest 0 001 g

7 14 Hot Block that is able to maintain temperature of 100 Celsius

8 STANDARDS, REAGENTS AND CONSUMABLE MATERIALS

8 1 Document all reagent and acid preparation information in a logbook, including acids and acid mixtures Label all reagents and acids/mixtures with appropriate identification, tracking , and expiration date information

8 2 Reagent water Water in which mercury is not detected by this method, 18-megaohm ultra-pure deionized water starting from a pre-purified (laboratory DI water) source

8 3 Argon Grade 5 0 (ultra high-purity, GC grade) inert gas that has been further purified by the removal of Hg using a gold-coated sand trap

8 4 Hydrochloric acid trace-metal purified reagent HCl containing less than 5 pg/mL Hg

8 5 Hydroxylamine hydrochloride Dissolve 150 g of NH_2OH HCl in reagent water and bring to 500 mL This solution may be purified by the addition of 0 5 mL of $SnCl_2$ solution and purging overnight at 350 mL/min with Hg-free Ar Store tightly capped

8 6 Stannous chloride Bring 100 g of $SnCl_2$ $2H_2O$ and 50 mL concentrated HCl to 500 mL with reagent water Purge overnight with mercury-free Ar at 350 mL/min to remove all traces of Hg. Store tightly capped.

UNCONTROLLED

8 7 Bromine monochloride (BrCl) Dissolve 5 4 g of reagent grade KBr in 500 mL of low-Hg HCl Place a clean magnetic stir bar in the bottle and stir for approximately 1 hr in a fume hood Slowly add 7 6 g reagent grade $KBrO_3$ to the acid with stirring When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange Loosely cap the bottle and allow to stir another hour before tightening the lid KBr and $KBrO_3$ are purified by heating to 250°C overnight in an oven

CAUTION This process generates copious quantities of free halogens (Cl_2 Br_2 BrCl) which are released from the bottle Add the $KBrO_3$ SLOWLY in a fume hood!

COPY

8 8 HNO_3/H_2SO_4 solution In a fume hood slowly add 300ml of concentrate H_2SO_4 to 700ml of concentrate HNO_3 in a Teflon bottle

Warning This mixture get hot and emits fumes

8 9 0 02 N Bromine monochloride solution Dilute 100mls of concentrated BrCl solution to 1000ml with reagent water in a Teflon bottle

8 10 Stock mercury standard Stock mercury standards (1 000 ppm) are obtained from CPI International, Santa Rosa, CA, P/N 4400-1000331 and Inorganics Ventures Inc Lakewood, NJ P/N CGHG1-5 A NIST-certified 10 000 ppm aqueous Hg solution (NBS-3133) is also available These solutions are stable until the expiration date

8 11 Secondary Hg standard Dilute 0 100 mL of the stock solution (1 000 ppm) to 100 mL in water containing 1 0 mL of BrCl This solution contains 1 00 ug/mL (1 00 ppm) Hg Keep in a tightly closed fluoropolymer bottle This expiration date is the same as the stock standard

8 12 Working Hg standard A Dilute 1 00 mL of the secondary Hg standard to 100 mL in a class A volumetric flask with reagent water containing 1 0% by volume BrCl solution This solution contains 10 0 ng/mL and should be replaced monthly

8 13 Working Hg standard B Dilute 0 100 mL of the secondary Hg standard to 1000 mL with reagent water containing 1 0% by volume BrCl solution (10 mL BrCl/1000mL) This solution contains 0 1 ng/mL and should be replaced monthly

9 PREVENTIVE MAINTENANCE

9 1 All maintenance activities are recorded in a maintenance logbook kept for each instrument

UNCONTROLLED

9 2 Broad or asymmetrical peaks indicate a problem with the desorption train, such as low gas flow rate, water vapor on the trap(s), or an analytical column damaged by chemical fumes or overheating

9 3 Damage to a trap is also indicated by a sharp peak followed by a small, broad peak

9 4 If the trap has been damaged, it and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration on downstream surfaces

9 5 Gold traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded

COPY

10 RESPONSIBILITIES

10 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP The acceptance criteria for test performance are listed in Table 1 Final review and sign-off of the data is performed by the department supervisor/manager or designee

10 2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency

11 PROCEDURE

11 1 An analytical batch is up to 20 field samples that are oxidized with the same reagents and analyzed within the same 12-hour shift The analytical batch contains the following standards, samples, and blanks in order

UNCONTROLLED COPY

Water Run

Water blank 1
Water blank 2
Method blank 1
Method blank 2
5 ng/L opr and bubbler blank
5 ng/L QCS and bubbler blank
up to 10 samples
Matrix Spike
Duplicate Matrix Spike
OPR (optional)
Up to 10 additional samples
Matrix Spike
Duplicate Matrix Spike
Method blank 3
5 ng/L OPR and bubbler blank

Soil Run

Calibration Verification (VER) and bubbler blank
Method Blank 1
Method Blank 2
OPR (use to demonstrate end to end analytical system)
QCS or SRM
up to 10 samples
Matrix Spike
Duplicate Matrix Spike
Calibration Verification (VER) and bubbler blank
Up to 10 additional samples
Matrix Spike
Duplicate Matrix Spike
Method blank 3
OPR (use to demonstrate end to end analytical system)
Calibration Verification (VER) and bubbler blank

For more than 20 samples in a 12 hour shift the sequence is repeated

11 2 Reagent blanks are analyzed in triplicate when there is a change in reagent(s) The average of these values is used to correct the sample reading for the contribution of the reagents to the measured mercury

11 3 Sample Preparation

11 3 1 Record all sample preparation and sample information on the applicable benchsheet This includes acid mixture tracking documentation

11 3 2 Water samples may be preserved with 5ml/L BrCl, more may be required for complete preservation, an aliquot of 100mls may be added directly to bubbler If more BrCl is used for the sample than 5ml/L, a method blank is prepared at the same level to be analyzed with that sample If not pour a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL HDPE bottle If estimated concentration is known, less sample may be used to keep the measured amount under 20ng (200 ng/L) Add bromine monochloride (BrCl), cap the bottle and digest at room temperature for 12 hours (Shorter digestion times can be achieved by using elevated temperatures For example, 70°C for 2 hours is adequate

UNCONTROLLED

11 3 3 For clear water and filtered samples, add 0 5 mL of BrCl for brown water and turbid samples, add 1 0 mL of BrCl If the yellow color disappears because of consumption by organic matter or sulfides, dilute the sample To minimize the contribution of background Hg, do not use more than 2 0 mL of the BrCl to oxidize the sample rather dilute the sample until a permanent (12-hr) yellow color is obtained with 2 0 mL of BrCl or less

COPY

11 3 4 Some highly organic matrices, such as sewage effluent will require dilution as much as 1 10 and longer oxidation times, or elevated temperatures (i e place sealed bottles in oven at 70°C for 2 hr) The oxidation must be continued until excess BrCl remains This can be checked using starch-iodide paper

11 3 5 Solid samples are prepared by weighing 400mg of sample into a 40ml vial To each sample, add 10 0 ml of HNO_3/H_2SO_4 solution A glass tapered marble placed over the digestion vessel Samples are allowed to sit for 1 hour at room temperature The samples are than placed in a Hot Block at 100° C for 2-3 hours refluxing Once the samples have cooled they are diluted to 40 mL with 0 02 N BrCl solution The samples then need to sit for At least 4 hours prior to analysis This is to allow for complete oxidation of the methyl Hg

11 3 6 Matrix spikes and matrix spike duplicates For each batch of 10 or fewer samples aliquot two additional 100-mL portions from a randomly selected sample spike at the level specified in Section 12 3 3, and process in the same manner as the samples

11 3 7 Method Blank If samples are being preserved with BrCl then three method blanks are prepared at the beginning of that week to represent the samples prepared that week If samples weren't preserved with BrCl, than three method blanks are prepared for every 20 or fewer, samples by adding BrCl (0 5 mL) to 100 mL of

deionized water The method blank uses bottles chosen at random from all sample bottles and serves as a check on the bottle washing procedure

11 3 8 Water blank At the same time as the samples are prepared, prepare a two water blanks by adding 0 5 mL of BrCl to 100 mL of DI water The water blanks use bottles designated for this purpose and this serves as a check on the mercury content of the water and reagents The mercury content of the water blank is used to correct the OPR, QCS, method blank values and dilutions

11 4 At the beginning of each 12 hour shift, attach lime traps to the bubbler and purge with Ar for 45-60 minutes to clean

UNCONTROLLED

11 5 Instrument Initialization--Allow the instrument to warm-up for 30 minutes before attempting to analyze samples.

***NOTE** Purging of halogens onto the gold trap will result in damage and low or irreproducible results*

11 6 Sample Analysis

11 6 1 Water Samples

COPY

11 6 1 1 Just prior to analysis, add 0 2 mL of NH_2OH to the BrCl-oxidized sample Cap the bottle and swirl the sample The yellow color will disappear indicating the destruction of the BrCl Allow the sample to react for 5 min with periodic swirling to be sure that no traces of halogens remain

11 6 1 2 Connect a lime trap and a gold trap to the bubbler, add 0 5 mL of $SnCl_2$ solution to the bubbler pour the reduced sample into the bubbler, and purge the sample with Ar for 20 min at 300-400 mL/min At the end of the sparging time, remove the gold trap, plug the ends and save for analysis (See Section 11 7) Use the Bubbler blanks to correct the sample measurements and the water blank to correct the QCS, OPR, and Method Blank measurements Remove the lime trap and rinse the sparging tube with deionized water If necessary, use acetone to remove moisture from the upper portion of the sparging tube It is important to make sure that the top of the sparging tube is dry for the next sample Leave the nitrogen on while performing this procedure Discard the water in the bubbler Rinse the bottom half of the bubbler with deionized water Close the nitrogen valve before adding the next sample to the bubbler

11 6 1 3 Repeat 11 6 1 1 and 11 6 1 2 for each standard, blank, QC sample and field sample

11 6 2 Solid samples - A 100ml portion of water is pre-purged with 0 5ml $SnCl_2$ solution for 5 minutes This is required for all samples and standards that are purged Connect a lime trap and a gold trap to the bubbler A VER is ran every ten samples and at the beginning and end of the run A 5ml aliquot of the samples and standards are purged for 20 min at 300-400 ml/min They are sparged according to the run order (See Section 11 1) At the end of the sparging time remove the gold trap, plug the ends and save for analysis (See Section 11 7) Use the Bubbler blanks to correct the sample measurements

11 7 Desorption of Hg from the gold trap

11 7.1 Remove the plugs from the gold trap, place the Nichrome wire coil around the trap and connect it into the analyzer train between the incoming Hg-free argon and the detector

UNCONTROLLED

11 7 2 Pass argon through the trap at a flow rate of approximately 30 mL/min for 45-60 seconds to drive off condensed water vapor

11 7 3 Apply electrical current (9 5-10 V DC) to the Nichrome coil around the gold trap and begin data collection The applied electrical current will thermally desorb the Hg (as Hg(0)) from the trap into the detector

11 7 4 After the 3-min desorption time, stop data collection turn off the current to the coil, and cool the trap (about one minute) using the cooling fan

COPY

11 8 Place the next gold trap in line and proceed with analysis of the next sample

Peaks generated using this technique should be very sharp and almost symmetrical Mercury elutes at approximately 2 min and has a width at half-height of about 11 seconds

11 9 Calibration and standardization

11 9 1 The calibration must contain five or more non-zero points and the results of the analysis of 3 bubbler blanks The lowest calibration point must be equivalent to the MRL or lower

11 9 2 Using the procedure in Section 11 7 standards are analyzed by the addition of aliquots of Hg working standard A (8 10) and Hg working standard B (8 11) directly into 100 mL of previously purged water in the bubbler Add 0 5 mL and 2 0 mL of working standard B and 0 5 mL $SnCl_2$ to the bubbler Swirl to produce a standard of 0 5 and 2 0 ng/L Purge under the normal operating conditions described above Sequentially follow with the addition of aliquots of 0 05, 0 20

0 50 and 2 0 mL of working standard A plus 0 5 mL of $SnCl_2$ to produce standards of 5 0, 25 0 50 0 and 200 0 ng/L

11 9 3 For each point subtract the mean peak area of the bubbler blanks for the batch from the area of each standard Calculate the calibration factors (CF) for Hg in each of the six standards as follows

$$CF = \frac{(C_s)}{(A_{Corr})}$$

where C_s = Concentration of the standard
A_{corr} = Bubbler blank corrected peak area

UNCONTROLLED

Calculate the relative standard deviation (RSD) of the calibration factor over the six-point range

11 9 4 Calibration criteria are as follows

(a) There must be a minimum of five non-zero calibration points
(b) The difference between successive calibration points must be no greater than a factor of 10 and no less than a factor of 2 and should be approximately evenly spaced on a logarithmic scale over the calibration range
(c) The relative standard deviation (RSD) of the calibration factors for all calibration points must be less than 15%
(d) The calibration factor for any calibration point at a concentration greater than 100 ng/L must be within ±15% of the average calibration factor for the points at or below 100
(e) The calibration factor for any point <0 5 ng/L must be within 25% of the average calibration factor for all points
(f) If calibration is to a higher range and this procedure is used for regulatory compliance, the ML must be less than one-third the regulatory compliance limit

COPY

11 9 5 Ongoing precision and recovery—Perform the ongoing precision and recovery test (12 3 1) to verify calibration prior to, and after in each analytical batch

12 QA/QC REQUIREMENTS

12 1 Initial demonstration of capability

12 1 1 Laboratory performance is compared to the established performance criteria listed in Table 1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method This ability is established as follows

12 1 2 Initial precision and recovery (IPR) To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations

12 1 2 1 Analyze four replicates of the working Hg standard (Section 8 10) according to the procedure beginning in Section 11 3 – 11 7 These four replicates are prepared the same as samples are prepared

12 1 2 2 Using the results of the set of four analyses compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for total Hg

12 1 2 3 Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and sample analysis may begin If however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable Correct the problem and repeat the test

UNCONTROLLED COPY

12 2 Method Detection Limits

12 2 1 A method detection limit (MDL) study must be undertaken before analysis of samples begins To establish detection limits that are precise and accurate the analyst must perform the following procedure Spike a minimum of seven blank replicates with a MDL spiking solution (at or below the MRL) and analyze Refer to the CAS *SOP for The Determination of Method Detection Limits and Limits of Detection*

12 2 2 Calculate the average concentration found (x) in the sample concentration and the standard deviation of the concentrations for each analyte Calculate the MDL for each analyte using the correct T value for the number of replicates The MDL study should be done annually

12 3 Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual in the *SOP for Sample Batches*, and in method 1631E An analytical batch is a set of samples oxidized with the same batch of reagents and analyzed during the same 12-hour shift A batch may be from 1 to 20 samples Each batch must be accompanied by three method blanks two OPR samples, and a QCS In addition, there must be one MS/MSD pair analyzed for every 10 samples

12 3 1 Ongoing precision and recovery (OPR) To demonstrate that the analysis system is in control and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations

12 3 1 1 Analyze the low-level Hg (5 ppt) working standard (Section 8 10) blank before and after analysis of each analytical batch according to the

procedure beginning in Section 11 Subtract the mean peak area of the bubbler blank and water blanks from the area for the standard and compute the concentration for the blank-subtracted standard

12 3 1 2 Run a bubbler blank after each OPR and QCS sample There must be at least 3 per analytical batch of 20 samples See section 12 4 4 1

12 3 1 3 Compare the concentration with the limits for ongoing precision and recovery in Table 1 If the concentration is in the range specified the analysis system is in control and analysis of samples and blanks may proceed If however the concentration is not in the specified range the analytical process is not in control. Correct the problem and repeat the ongoing precision and recovery test

UNCONTROLLED

12 3 2 Quality control sample (QCS) A QCS from a source different than the Hg used to produce the standards (OPR and working standards) must be analyzed at the beginning of each analytical batch The acceptance criteria for the water QCS is 77-123% For soils, a reference material routinely used and the acceptance criterion is the known concentration range provided with the material If project-specified, a spiked blank matrix (Teflon beads) is used for the solid QCS, in which case the acceptance limits are 70-130%

12 3 3 Matrix spike (MS) and matrix spike duplicate (MSD)

COPY

12 3 3 1 To assess the performance of the method on a given sample matrix, spike in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge Blanks (e g field blanks) may not be used for MS/MSD analysis A spike level of 5 ng/L has been found to acceptable for most samples

Note If as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit the spiking level shall be at that limit or at 1-5 times the background concentration in the sample, whichever is greater If the sample concentration is not being checked against a regulatory limit the spike shall be at 1-5 times the background concentration in the sample

12 3 3 2 Spike two sample aliquots (MS and MSD) with the spiking solution and analyze these aliquots to determine the concentration after spiking (A)

12 3 3 3 Calculate the percent recovery (P) in each aliquot using the following equation

100 (A-B)/T

where
A = Measured concentration of analyte after spiking
B = Measured concentration of analyte before spiking
T = True concentration of the spike

12 3 3 4 Compare the percent recovery with the QC acceptance criteria in Table 1 If the results of spike fail the acceptance criteria, and recovery for the OPR standard for the analytical batch is within the acceptance criteria in Table 1 an interference may be present The result may not be reported for regulatory compliance purposes If the interference can be attributed to sampling the site or discharge should be re-sampled If the interference can be attributed to a laboratory error or deficiency, the analyst must take corrective action and repeat analysis of the associated samples (10 per MS/MSD pair) and MS/MSD

UNCONTROLLED

12 3 3 5 If the results of both the spike and the OPR test fail the acceptance criteria, the analytical system is judged to be out of control The analyst must identify and correct the problem and reanalyze the sample batch

12 3 3 6 Relative percent difference between duplicates Compute the relative percent difference (RPD) between the MS and MSD according to the following equation using the concentrations found in the MS and MSD Do not use the recoveries calculated in Section 12 4 4 3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration

COPY

$$RPD = 200 \times (D1-D2)/(D1+D2)$$

Where

Dl = concentration of Hg in the MS sample
D2 = concentration of Hg in the MSD sample

The RPD for the MS/MSD pair shall meet the acceptance criterion in Table 1 If the criterion is not met the system is judged to be out of control The problem must immediately be identified and corrected, and the analytical batch reanalyzed

12 3 4 Blanks—Blanks are critical to the reliable determination of Hg at low levels The sections below give the minimum requirements for analysis of blanks

12 3 4 1 Bubbler blanks—Bubbler blanks are analyzed to demonstrate freedom from system contamination At least three bubbler blanks must be run per analytical batch One bubbler blank must be analyzed following each OPR

12 3 4 1 1 Immediately after analyzing a sample for Hg place a clean gold trap on the bubbler purge and analyze the sample a second time using the procedure in Section 11 and determine the amount of Hg remaining in the system

12 3 4 1 2 If the bubbler blank is found to contain more than 50 pg Hg the system is out of control The problem must be investigated and remedied, and the samples run on that bubbler must be reanalyzed If the blanks from other bubblers contain less than 50 pg Hg the data associated with those bubblers remain valid

UNCONTROLLED

12 3 4 1 3 The mean result for all bubbler blanks (from bubblers passing the specification above) in an analytical batch (at least three bubbler blanks) is calculated at the end of the batch The mean result must be < 25 pg with a standard deviation of < 10 pg for the batch to be considered valid

12 3 4 1 4 If Hg in the bubbler blank exceeds the acceptance criteria, the system is out of control, and the problem must be resolved and the samples reanalyzed. Usually, the bubbler blank is too high for one of the following reasons

COPY

- Bubblers need rigorous cleaning,
- Soda-lime is contaminated or
- Carrier gas is contaminated

12 3 4 2 Method Blank At the same time as the samples are prepared, prepare three method blanks for every 20 or fewer samples prepared by adding BrCl (0 5 mL) to 100 mL of deionized water Four method blanks are prepared by adding 2 5ml/500ml in a clean sample bottles to represent samples that are preserved for that week When samples require more BrCl for preservation than a method blank at the same level is prepared to accompany those samples for analysis The method blank uses bottles chosen at random from all sample bottles and serves as a check on the bottle washing procedure

12 3 4 3 Water blank At the same time as the samples are prepared, prepare 2 water blanks by adding 0 5 mL of BrCl to 100 mL of DI water The water blanks use bottles designated for this purpose and this serves as a check on the mercury content of the water and reagents The mercury content of the

water blank is used to correct the OPR, QCS, and Method Blank values One water blank is prepared at the beginning of purging samples

12 4 Reagent blanks—The Hg concentration in reagent blanks must be determined on solutions of reagents by adding these reagents to reagent water in the bubbler

12 4 1 Reagent blanks are required when the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are prepared, with verification in triplicate for each new batch of reagents is needed

12 4 2 Add aliquots of BrCl (0 5 mL), NH_2 OH (0 2 mL) and $SnCl_2$ (0 5 mL) to previously purged water in the bubbler In order to evaluate the reagents as a potential source of contamination, the amount of reagent added to the reagent blank(s) must be the same as the amount of reagent added to the sample(s)

UNCONTROLLED

12 4 3 The presence of more than 20 pg of Hg indicates a problem with the reagent solution The purging of certain reagent solutions such as $SnCl_2$ or NH_2 OH with mercury-free argon can reduce Hg to acceptable levels Because BrCl cannot be purified a new batch should be made from different reagents and should be tested for Hg levels if the level of Hg in the BrCl solution is too high

12 5 Bottle blanks—After undergoing the cleaning procedures in this Method bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures A representative set of sample bottles should be filled with reagent water acidified to pH <2 and allowed to stand for a minimum of 24 h Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle After standing, the water should be analyzed for any signs of contamination If a bottle shows contamination at or above the level specified for the field blank the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles re-cleaned

COPY

12 6 As part of the QC program for the laboratory method precision and accuracy for samples should be assessed and records maintained Update the accuracy assessment regularly

13 DATA REDUCTION, REVIEW, AND REPORTING

13 1 It is the analysts responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run Results for QC analyses are calculated and recorded as specified in section 12

13 2 Quantitation

13 2 1 Calculate the concentration of Hg in each sample directly from the mean calibration factor

$$Hg(ng/L) = \frac{(A_s - \overline{A}_{BB}) \times CF_m}{V}$$

where A_s = peak area (or height) for Hg in sample
A_{BB} = peak area (or height) for Hg in bubbler blank (mean)
CF_m = Mean calibration factor
V = Volume of sample

UNCONTROLLED

13.2.2 Report results for Hg in reagent blanks separately

13 3 Report results for samples in ng/L to two significant figures (three if >10 ng/L) for total Hg found above the MRL (See Table 1) Report results below the MRL but above the MDL as estimated values (J flagged) Report results below the MRL as ND, unless the project specifies reporting to the MDL

13 4 If the result over the calibration range prepare and analyze a diluted sample using the appropriate dilution factor to bring within range For water samples, dilute the selected sample aliquot in reagent water and analyze For soils, dilute an appropriate smaller aliquot of the soil digestate into reagent water and analyze For samples far over range, an alternate procedure may be more appropriate Consult with the Project Chemist before using another method

COPY

13 5 The data packet for the sequence is submitted for review by supervisor or designee The results are transferred to the appropriate report form located in the CAS network directory R \ICP\WIP Once the results are transferred, the report is reviewed

13 6 Refer to the *SOP for Laboratory Data Review Process* for general instructions for data review

14 METHOD PERFORMANCE

14 1 This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

14 2 The method detection limit (MDL) is established using the procedure described in the SOP for *The Determination of Method Detection Limits and Limits of Detection* (ADM-MDL) Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual

15 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also, refer to the *SOP for Corrective Action* for correct procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the *SOP for Report Generation* or in project-specific requirements

16 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly

UNCONTROLLED

17 WASTE MANAGEMENT

17 1 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual

17 2 This method uses acid Waste acid is hazardous to the sewer system and to the environment All acid waste must be neutralized to a pH of 2 5-12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record See the CAS EH&S Manual for details

COPY

18 TRAINING

18 1 Refer to the *SOP for Documentation of Training* for standard procedures

18 2 Training outline

18 2 1 Review literature (see references section) Read and understand the SOP Also review the applicable MSDS for all reagents and standards used Following these reviews, observe the procedure as performed by an experienced analyst at least three times

18 2 2 The next training step is to assist in the procedure under the guidance of an experienced analyst During this period, the analyst is expected to transition from a role of assisting to performing the procedure with minimal oversight from an experienced analyst

18 2 3 Perform initial precision and recovery (IPR) study as described above for water samples Summaries of the IPR are reviewed and signed by the supervisor Copies may be forwarded to the employee's training file For applicable tests IPR studies should be performed in order to be equivalent to NELAC s Initial Demonstration of Capability

18 3 Training is documented following the *SOP for Documentation of Training*

NOTE When the analyst training is documented by the supervisor on internal training documentation forms the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently

UNCONTROLLED

19 REFERENCES

19 1 *Mercury in Water by Oxidation Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry* Method 1631, Revision E, USEPA, August 2002

COPY

Table 1

Acceptance Criteria for Test Performance

Acceptance Criterion	Criteria
Method Detection Limit	0 08 ng/L[a]
Method Reporting Limit	1 ng/L[b]
Initial Precision and Recovery	
Precision (s)	± 21%
Recovery	79-121%
Interlaboratory Comparison	75-125%
Matrix Spike/Matrix Spike Duplicate	
Recovery	71-125%
Relative Percent Difference	± 24%
Ongoing Precision and Recovery	77-123%

UNCONTROLLED

a Method 1631E states that the method detection limit has been determined to be 0 2 ng/L when no interferences are present

b Method 1631E states "the minimum level of quantitation (ML) has been established as 0 5 ng/L " The MDL and calibration can support the use of a 0 5 ng/L MRL if required by regulation or project protocols With use of an additional calibration standard the range may be extended to 200 ng/L if necessary.

COPY

STANDARD OPERATING PROCEDURE

for

METHYL MERCURY IN WATER BY DISTILLATION, AQUEOUS ETHYLATION, PURGE AND TRAP, AND CVAFS

SOP No MET-1630W

Revision 1

September 1, 2009

UNCONTROLLED

Approved by _____ Supervisor _____ Date 9/1/09

_____ QA Manager _____ Date 9/1/09

_____ Laboratory Manager _____ Date 9/1/09

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso Washington 98626

© Columbia Analytical Services Inc 2009

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

METHYL MERCURY IN WATER BY DISTILLATION, AQUEOUS ETHYLATION, PURGE AND TRAP, AND CVAFS

1 SCOPE AND APPLICATION

1 1 This method is for determination of methyl mercury (CH_3Hg) in filtered and unfiltered water by distillation aqueous ethylation purge and trap desorption and cold-vapor atomic fluorescence spectrometry (CVAFS) The method is for the determination of CH3Hg in aqueous samples, ranging from sea water to sewage effluent based on EPA 1630

1 2 This method is designed for determination of CH_3Hg in the range of 0 02-5 ng/L and may be extended to higher levels by selection of a smaller sample size

UNCONTROLLED

1 3 Methyl mercury as defined in this method means all methyl mercury forms and species found in the sample such as CH_3Hg+ CH_3HgCl CH_3HgOH and CH_3HgS-R

1 4 The detection limit and minimum level of quantitation in this method are usually dependent on the level of background elements rather than instrumental limitations The method detection limit (MDL 40 CFR 136 Appendix B) for CH_3Hg has been determined to be 0 02 ng/L when no background elements or interferences are present The minimum level (ML) has been established as 0 06 ng/L

COPY

2 METHOD SUMMARY

2 1 A 100-2000 mL sample is collected directly into specially cleaned pretested fluoropolymer or borosilicate bottle(s) using sample handling techniques specially designed for collection of metals at trace levels

2 2 For dissolved CH_3Hg samples are filtered through a 0 45-µm capsule filter

2 3 Fresh water samples are preserved by adding 4-5 mL/L of pretested 11 6 M HCl while saline samples ([Cl-] > 500 ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution to avoid distillation interferences caused by excess chloride

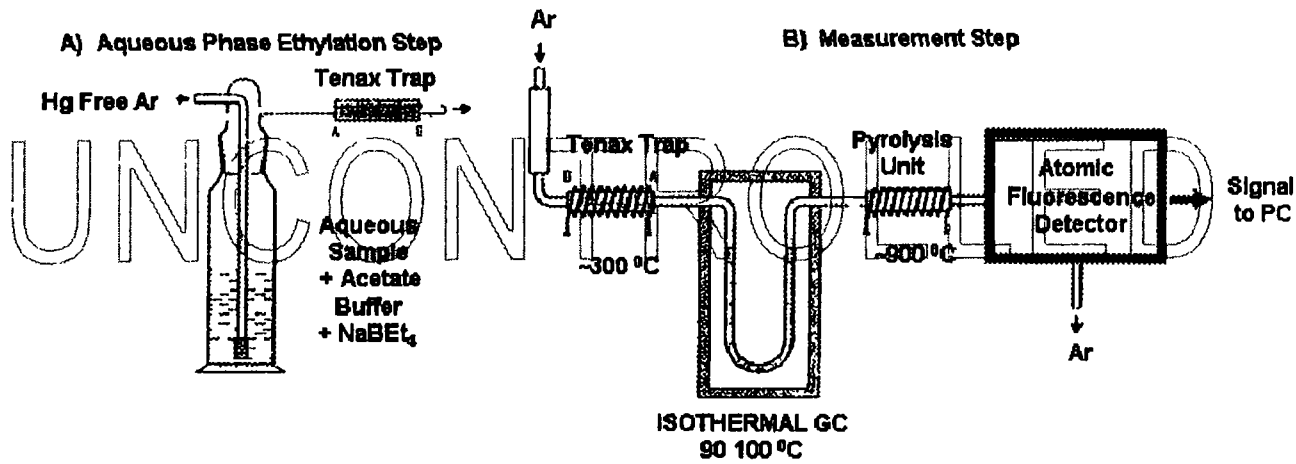
2 4 Prior to analysis a 45-mL sample aliquot is placed in a specially designed fluoropolymer distillation vessel and ~ 35 mL of the water is distilled into the receiving vessel at 125°C under Argon flow

2 5 After distillation the sample is adjusted to ~ pH 4 9 with an acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate (STEB or $NaBEt_4$)

2 6 The ethyl analog of CH_3Hg methylethyl mercury (CH_3CH_2 -Hg-CH_3) is separated from solution by purging with Argon onto a Tenax ® trap

2 7 The trapped methylethyl mercury (MeEtHg) is thermally desorbed from the trap via argon that carries the desorbed organo-mercurials through a GC column, then onto a pyrolytic decomposition column which converts organo-mercurial forms to elemental mercury (Hg^0) and finally into the cold vapor atomic fluorescence spectrometer (CVAFS) for detection

Figure 1 Schematic of Apparatus



UNCONTROLLED COPY

3 DEFINITIONS

3 1 **Dissolved Methyl Mercury** - All distillable CH3Hg forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45 micron filter

3 2 **Methyl Mercury** - Mono Methylmercury = MMHg = Methyl Mercury = MeHg = CH_3Hg All acid-distillable Hg, which, upon reaction with NaBEt4 yields methylethyl mercury This includes but is not limited to CH_3Hg^+ strongly organo-complexed CH_3Hg compounds adsorbed particulate CH_3Hg, and CH_3Hg bound in microorganisms In freshly collected samples dimethyl mercury ($(CH_3)_2Hg$) will not be recovered as CH_3Hg, but in samples which have been acidified for several days most $(CH_3)_2Hg$ has broken down to CH_3Hg In this method, CH_3Hg and total recoverable CH_3Hg are synonymous

3 3 **Analysis Sequence** - Samples are analyzed in a set referred to as an analysis sequence The sequence begins with instrument calibration followed by sample analyses interspersed with various quality control checks The sequence is ≤ 20 samples and concurrent QC checks

3 4 **Ethylation Blank** – A minimum of one Ethylation blank is run for each calibration curve The ethylation blank is run on clean DIH_2O exactly as standards (i e with acetate buffer and ethylating reagent and purged onto a trap) The peak height or area of the ethylation blank (or mean of multiple ethylation blanks) is subtracted from the area of each standard to establish the calibration factors

3 5 **Ethylating Agent** – Sodium Tetra Ethyl Borate or STEB or $NaBEt_4$

3 6 **Matrix Spike** (MS) - In the matrix spike analysis a predetermined quantity of standard solution of analyte is added to a sample matrix prior to sample preparation and analysis The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for analyses Percent recoveries are calculated for the analyte detected

3 7 **Matrix Spike Duplicate** (MSD) - In the matrix spike duplicate analysis a duplicate predetermined quantity of standard solution of analyte is added to a sample matrix prior to sample preparation and analysis The purpose of the matrix spike duplicate is to evaluate the effects of the sample matrix on the method used for analyses Percent recoveries are calculated for the analyte detected The relative percent difference (RPD) between the matrix spike and matrix spike duplicate is calculated and used to assess analytical precision

UNCONTROLLED

3 8 **Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process The method blank consists of all reagents, carried through the entire analytical procedure Either the concentration or peak height of the method blank is subtracted from the concentration or peak height of the samples, before calculating sample concentrations

3 9 **Quality Control Sample (QCS)** A sample containing CH_3Hg at known concentrations The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards It is used as an independent check of instrument calibration and is not carried through the whole method, but just ethylated as the calibration standards are

COPY

3 10 **Ongoing Precision Recovery (OPR)** - A standard analyzed at the beginning and end of an analytical sequence The spiked standard is carried through the whole method and is used to verify the ongoing validity of the method

3 11 **Standard Reference Material (SRM)** - A sample with a certified concentration

4 INTERFERENCES

4 1 Extreme care must be used in preventing ambient water samples from becoming contaminated during the sampling and analysis process Samples may become contaminated by numerous routes Potential sources of trace metal contamination during sampling include metallic or metal-containing labware (e g talc gloves that contain high levels of zinc) containers sampling equipment reagents and reagent water improperly cleaned and stored equipment labware and reagents and atmospheric inputs such as dirt and dust Even human contact can be a source of trace metal contamination For example it has been demonstrated that dental work (e g , mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation

4 2 Contamination Control Philosophy—The best way to control contamination is to completely avoid exposure of samples to contamination in the first place Avoiding exposure means performing operations in an area free from contamination Two of the most important factors in avoiding/reducing contamination are (1) an awareness of potential sources of contamination and (2) strict attention to the work being done It is imperative that the procedures described in this method be carried out by well-trained experienced personnel

4 2 1 Use a clean environment—The ideal environment for processing samples is a class 100 clean room If a clean room is not available all sample preparation should be performed in a class 100 clean bench or a nonmetal glove box fed by mercury-free and particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally in the clean room

UNCONTROLLED

4 2 2 Minimize exposure—The apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized When not in use the Apparatus should be covered with clean plastic wrap stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags

4 2 3 Clean work surfaces—Before a given batch of samples is processed all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water

COPY

4 2 4 Wear gloves—Sampling personnel must wear clean non talc gloves during all operations involving handling of the Apparatus samples, and blanks Only clean gloves may touch the apparatus If another object or substance is touched the glove(s) must be changed before again handling the apparatus If it is even suspected that gloves have become contaminated work must be halted the contaminated gloves removed, and a new pair of clean gloves put on

4 2 5 Use metal-free apparatus—All apparatus used for determination of CH_3Hg at ambient water quality criteria levels must be nonmetallic and free of material that may contain metals

4 2 6 Construction materials—Only fluoropolymer or borosilicate glass containers should be used for samples that will be analyzed for Hg because Hg vapors can diffuse in or out of other materials resulting in results that are biased low or high All materials regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures in this method and must be known to be clean and mercury free before proceeding

4 2 7 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of apparatus so that contamination can be traced and logbooks or spreadsheets should be maintained to track the sample from the container through the labware to introduction into the instrument It may be useful to dedicate separate sets of labware to different sample types e g receiving waters vs effluents However, the apparatus used for processing blanks and standards must be mixed with the apparatus used to process samples so that contamination of all labware can be detected

4 2 8 The laboratory or cleaning facility is responsible for cleaning the apparatus used by the sampling team If there are any indications that the apparatus is not clean when received by the sampling team (e g , ripped storage bags) an assessment of the likelihood of contamination must be made

UNCONTROLLED

4 2 9 Contamination by carryover—Contamination may occur when a sample containing a low concentration of CH_3Hg is processed immediately after a sample containing a relatively high concentration When an unusually concentrated sample is encountered an ethylation blank should be analyzed immediately following the sample to check for carryover Samples known or suspected to contain the lowest concentration of CH_3Hg should be analyzed first followed by samples containing higher levels

COPY

4 2 10 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates and other samples containing high concentrations of Hg or CH_3Hg are processed and analyzed This method is not intended for application to these samples and samples containing high concentrations of trace metals should not be permitted into the clean room and laboratory dedicated for processing trace metals samples

4 2 11 Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination For example clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample Therefore it is imperative that every piece of the apparatus that is directly or indirectly used in the collection processing and analysis of samples be thoroughly cleaned

4 2 12 Contamination by airborne particulate matter—Airborne particles are less obvious substances capable of contaminating samples Samples may be contaminated by airborne dust dirt particles or vapors from unfiltered air supplies nearby corroded or rusted pipes, wires or other fixtures or metal-containing paint Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination

4 3 Interferences

4 3 1 Metals Iron and Sulfur may cause interferences

4 3 2 Chloride Distillation of CH_3Hg from solution requires a carefully controlled level of HCl in solution Distillation will not be quantitative if too little HCl is added but too much HCl results in co-distillation of HCl fumes which interfere with the ethylation procedure Therefore fresh water samples must be preserved only with between 0 3% and 0 5% (v/v) 11 6 M HCl and salt water samples with between 0 1% and 0 2% (v/v) 9 M H_2SO_4

UNCONTROLLED

4 3 3 Nitric Acid Samples preserved with nitric acid (HNO_3) cannot be analyzed for CH_3Hg as the analyte is partially decomposed in the distillation step by this reagent

4 3 4 Molecular Interference The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms The Tenax® trap eliminates quenching due to trace gases but it still remains the analysts' responsibility to ensure high purity inert carrier gas and a leak-free analytical train In some rare cases (such as oil polluted water) low molecular weight organic compounds may purge with the methylethyl mercury and collect on the trap subsequently resulting in signal quenching during elution Such cases are best treated by sample dilution prior to distillation

COPY

4 3 5 Inorganic Mercury and TOC A positive artifact is possible with the distillation procedure in cases where high inorganic Hg concentrations are present (Reference 7 in Reference 1) In natural waters approximately 0 01 to 0 05% of the ambient inorganic Hg in solution may be methylated by ambient organic matter during the distillation step In most waters, where the percent CH_3Hg is 1-30% of the total this effect is trivial However, the analyst should be aware that in inorganic Hg contaminated waters the fraction CH_3Hg can be < 1% of the total and so flagging of the data (as representing a maximum estimate of CH_3Hg concentration) may be warranted In samples with high levels of divalent mercury (Hg II), solvent extraction may be preferable to distillation (Reference 7 in Reference 1)

5 SAFETY

5 1 All appropriate safety precautions for handling solvents reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment such as safety glasses lab coat, and the correct gloves

5 2 Chemicals reagents and standards must be handled as described in the CAS safety policies approved methods and in MSDSs where available Refer to the CAS Environmental Health and Safety Manual and the appropriate MSDS prior to beginning this method

5 3 Hydrochloric and Sulfuric Acids and Potassium Hydroxide are used in this method These acids and bases are extremely corrosive and care must be taken while handling them A face shield should be used while pouring acids Safety glasses lab coat and gloves should be worn while working with the solutions

5 4 Chronic mercury exposure may cause kidney damage, muscle tremors spasms personality changes depression, irritability, and nervousness Organo-mercurials may cause permanent brain damage Because of the toxicological and physical properties of the Hg pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and associated risks **High concentrations of methyl mercury can be fatal!**

UNCONTROLLED

5 5 CAS purchases a dilute standard solution of methyl mercury for this method If primary solutions are prepared, they must be prepared in a fume hood with the utmost caution

5 6 Hands should be washed thoroughly after each manipulation and before breaks

5 7 Ethylating agent ($NaBEt_4$) is toxic gives off toxic gases (triethylboron) and is spontaneously combustible To discard unused portions of ethylating agent and empty bottles place into a large beaker of ~10% 1N HCl in the hood, triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid Leave the acid beaker in the hood indefinitely or boil down to half the original volume to destroy residues before discarding as acid waste

COPY

6 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6 1 Before samples are collected the type of data required (i e dissolved or total) so that appropriate preservation and pretreatment steps can be taken The pH of all aqueous samples must be tested immediately before removing an aliquot for processing or direct analysis to ensure the sample has been properly preserved

NOTE Do not dip pH paper or pH meter into the sample remove a small aliquot with a clean pipette and test the aliquot pH

6 2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps Borosilicate glass bottles may be used if Hg and Hg species are the only target analytes It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads **Polyethylene sample bottles must not be used**

NOTE Discrete samplers have been found to contaminate samples with Hg at the ng/L level therefore great care should be exercised if this type of sampler is used to collect

samples It may be necessary for the sampling team to use other means of sample collection if samples are found to be contaminated using the discrete sampler

6 3 Sample filtration—For dissolved CH3Hg samples and field blanks are filtered through a 0 45-µm capsule filter (Section 7 2) The Sampling Method describes filtering procedures

6 4 Preservation—Samples are preserved by adding 4-5 mL/L of concentrated HCL (to allow both CH_3Hg and total Hg determination) Saline samples ([Cl-]>500 ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution Acid-preserved samples are stable for at least six months if kept dark and cool

6 4 1 Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles (2) filled to the top with no head space, (3) capped tightly and (4) maintained at 0-4EC from the time of collection until preservation The samples must be acid-preserved within 48 h of sampling

UNCONTROLLED

6 4 2 Handling of the samples in the laboratory should be undertaken on a mercury-free clean bench

6 5 Storage—Sample bottles should be stored in clean (new) polyethylene bags until analysis To maintain CH_3Hg concentrations without degradation, it is necessary to keep acid-preserved samples dark and cool If properly preserved samples can be held up at least six months before analysis

COPY

7 APPARATUS AND EQUIPMENT

7 1 Cold vapor atomic fluorescence spectrometer (CVAFS) Brooks-Rand (Seattle WA) Model III CVAFS or equivalent

7 2 Filter 45-µm 15 mm diameter capsule filter (Gelman Supor 12175 or equivalent)

7 3 Flow meter/needle valve capable of reproducibly keeping carrier gas flow at 30 mL/min

7 4 Flow meter/needle valve capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min

7 5 Fluoropolymer fittings Connections between components and columns are made using 6 4-mm O D fluoropolymer tubing and fluoropolymer friction-fit or threaded connectors

7 6 Tenax® traps for Hg speciation Silanized blanked with ends plugged with Teflon 1/4" O D x 10 cm length (Brooks Rand AF-21-00 or equivalent)

7 7 Isothermal GC Unit The GC column is ~ 0 3 M long borosilicate glass column tubing with 0 25-in O D and 4-mm I D bore The column is silanized, and packed with preconditioned 60/80 mesh 15% OV-3 on Chromasorb WAW-DMSC held in place with silanized glass wool plugs The column is held in a small temperature-controlled isothermal oven made from a heating mantle (Supelco Inc custom product or from Brooks Rand

7 8 Pyrolytic Organo-mercury Breakdown Column A 20-cm length of 7-mm O D by 4 5-mm I D quartz tubing with the central 10 cm packed with quartz wool The column is wrapped with 10 cm of 22-gage Nichrome wire that is electrically heated to about 750-900 ^{0}C (bright orange) with ~56 volts from an autotransformer

UNCONTROLLED

7 9 Gold-coated sand trap or gold wire trap for removing mercury from argon line and for trapping mercury exiting the detector A tube 10-cm x 6 5-mm O D x 4-mm I D quartz tubing The tube is filled with 3 4 cm of gold-coated 45/60 mesh quartz sand with the ends plugged with quartz wool (Brooks Rand, Ltd , Seattle, WA, Part No AF-20 or equivalent)

7 10 Traps are fitted with 6 5-mm i d fluoropolymer friction-fit sleeves for making connection to the system When traps are not in use fluoropolymer end plugs are inserted in trap ends to eliminate contamination At least 16 traps are needed for efficient operation

7 11 Computer (Pentium or better) and Windows Mercury Guru software to record and integrate the signal from the spectrometer

COPY

7 12 Pipettors All-plastic pneumatic fixed-volume and variable pipettors 20 uL to 10 0 mL

7 13 Analytical balance capable of weighing to the nearest 0 0001 g

7 14 Oven able to maintain temperature of 70 to 100 Celsius

7 15 50 mL Teflon Bombs (Savillex or equivalent)

7 16 Ultra high-purity argon (grade 5 0)

7 17 Cold vapor generator (bubbler)—180 mL borosilicate glass with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0 2 cm of the bubbler bottom (Brooks Rand, Frontier Geosciences, Inc or equivalent)

8 STANDARDS, REAGENTS AND CONSUMABLE MATERIALS

8 1 Reagent water Water in which mercury is not detected by 1631 total mercury method 18-megaohm ultra-pure deionized water from a pre-purified (laboratory DI water) source

8 2 Argon Grade 5 0 (ultra high-purity, GC grade) inert gas that has been further purified by the removal of Hg using a gold-coated sand trap

8 3 Hydrochloric acid—Trace-metal purified reagent HCl containing less than 5 pg/mL Hg CH_3Hg is not stable in concentrated acid so the acid does not need to be tested for CH_3Hg

8 4 Sulfuric acid—Trace-metal purified reagent H_2SO_4 containing less than 5 pg/mL Hg CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH_3Hg

8 5 Glacial Acetic Acid Reagent grade Blank Pre-tested and verified to be low in mercury

UNCONTROLLED

8 6 Potassium Acetate Neat, reagent grade Blank Pre-tested and verified to be low in mercury

8 7 Potassium Hydroxide Neat pellets Semiconductor grade (or shown low in Hg)

8 8 Sodium Tetraethyl Borate 1-g vials **Use STREM as supplier**

8 9 APDC 1% Solution Weigh 0 1 – 0 2 g APDC (ammonium pyrrolidine dithiocarbamate) to the nearest mg into a 40 mL amber VOA vial Add water such that the total weight is now 100 times the starting weight, cap tightly and shake to dissolve The solution may be purified by extraction with three 10 mL aliquots of methylene chloride

COPY

NOTE This preparation is small and in amber to protect the APDC which is light reactive It is strongly recommended that the solution be prepared fresh daily

8 10 Ethylating Agent (Sodium Tetraethyl Borate 1% Solution STEB, $NaBEt_4$)

8 10 1 Rinse approximately 20 seven-milliliter Teflon vials with reagent water and arrange in a vial rack in a class-100 clean hood (Or use amber HPLC auto-sampler vials)

8 10 2 Pour 100 mL of reagent water into a 125-mL Teflon bottle and add 2 0 g of KOH pellets Dissolve mixture and place in freezer until ice crystals just begin to form

8 10 3 Turn on reagent water Remove wax and tape seal from a 1 0-g ampoule of sodium tetraethyl borate Open the ampoule and immediately transfer its contents to the 125-mL Teflon bottle cap tightly and give a few quick shakes

8 10 4 Fill the now empty ampoule and its cap with reagent water and sink into a beaker containing water and HCl (the pure borate powder is pyrophoric and could spontaneously-combust when exposed to air if not stabilized by the addition of water)

8 10 5 Shake the borate solution again then transfer to the vials, leaving ample air space for freezing and capping tightly

8 10 6 Place all the vials in the freezer standing upright

8 10 7 If any doubt arises about the quality of the ethylating reagent, make a new batch as old material often gives good results for reagent water spikes, but not for environmental samples, Do not use STEB solid or 1% solution if they have a yellow color

UNCONTROLLED

8 11 2M Acetate Buffer 2 M Acetate Buffer

8 11 1 Add 100 mL reagent water to a Teflon bottle

8 11 2 Add 19 6 g of Potassium Acetate

8 11 3 Add 11 8 mL of Glacial Acetic Acid

8 11 4 Ethylate with 0 5 mL STEB (1% solution) and purge overnight with argon to remove trace methyl mercury This solution has an indefinite lifetime when stored in Teflon

COPY

8 12 Argon (Ar) Use Grade 5 0 (ultra high purity grade) argon that has been further purified by the removal of mercury using a gold or iodated carbon trap that is located in line between the gas output and the analyzer gas input

8 13 Stock methylmercury standard Stock methylmercury standards (1 0 ug/mL= 1 000 ppm) are obtained from Brooks Rand Seattle Two standards are purchased The first is MeHgCl and the second (used for QCS) is from a second source and is MeHgOH Both standards are sold as 1 00 ug/L in 0 5% HOAc and 0 2% HCL (v/v) These solutions are kept in the refrigerator and are stable until the expiration date (one year)

8 14 MeHg standard A Pipette 0 100 mL of the stock solution (1ug/mL = 1 000 000 pg/mL) to 100 mL volumetric flask containing ~ 50 mL DIH_2O 0 5ml HOAc and 0 2 ml HCL QS with DIH_2O The resulting solution contains 1000 pg/mL MeHg Keep in a tightly closed Teflon bottle in the refrigerator This expiration date is the same as the stock standard

8 15 MeHg standard B Pipette 10 0 mL of MeHg STD B (1,000 pg/mL) to 100 mL volumetric flask containing ~ 50 mL DIH_2O, 0 5ml HOAc, and 0 2 ml HCL QS with DIH_2O The resulting solution contains 100 pg/mL MeHg Keep in a tightly closed Teflon bottle in the refrigerator This expiration date is the same as the stock standard

8 16 MeHg standard C Pipette 1 0 mL of MeHg STD B (1 000 pg/mL) to 100 mL volumetric flask containing ~ 50 mL DIH_2O 0 5ml HOAc and 0 2 ml HCL QS with DIH_2O The resulting solution contains 10 pg/mL MeHg Keep in a tightly closed Teflon bottle in the refrigerator This expiration date is the same as the stock standard

9 PREVENTIVE MAINTENANCE

UNCONTROLLED

9 1 All maintenance activities are recorded in a maintenance logbook kept for each instrument

9 2 Broad or asymmetrical peaks indicate a problem with the desorption train, such as low gas flow rate water vapor on the trap(s) or a GC column damaged by chemicals or overheating Replace or recondition traps and GC column as needed

9 3 Traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded Traps are best when blanked before each use in analysis

9 4 Bubblers must be kept clean by at least triple rinsing with / storing in DIH_2O between runs Make sure to fill and drain the dip tube during each rinse Alternatively store in dilute HCl

COPY

9 5 Occasionally move the Pyrolytic Coil off center (Right and Left) while blanking traps This is done to remove mercury from the sides of the Pyrolytic tube

9 6 Condition the GC column ~ every 2 to 3 months **SLOWLY** ramp the GC oven up to 180 ^{0}C and condition for 12-16 hours This purges impurities from the column See the Model III manual for this procedure

NOTE Ramping too quickly causes the oven to overshoot the desired temperature Going too high (200 ^{0}C) will ruin the column packing material

9 7 Depending on usage the Mercury Source Lamp in the CVASS unit will need to be changed This procedure is found in the Brooks Rand Manual

10 RESPONSIBILITIES

10 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP The acceptance criteria for test performance are listed in Table 1 This demonstration is in accordance with the training program of the

laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

10 2 It is the responsibility of the department supervisor/manager to document analyst training Documenting method proficiency, as described in the CAS SOP for Documentation of Training, is also the responsibility of the department supervisor/manager

11 PROCEDURE

11 1 An analytical batch is up to 20 field samples that are prepared with the same reagents and analyzed within the same 12-hour shift The analytical batch contains the following standards, samples, blanks, and QC checks

UNCONTROLLED

Method Blank 1
Method Blank 2
Method Blank 3
OPR (Carried through entire method)
Matrix Spike
Matrix Spike Duplicate
Up to 10 samples
QCS (2nd Source ethylated just as a standard)
Matrix Spike
Matrix Spike Duplicate
Up to 10 additional samples
OPR (Carried through entire method)

COPY

For more than 20 samples in a 12 hour shift the sequence is repeated Method blanks are analyzed in triplicate The average of these values is used to correct the sample reading for the contribution of the reagents and the prep tools/containers to the measured methylmercury in unknown samples The mean blank value should be less than 0 045 ng/L of CH_3Hg, and the variability should be less than 0 015 ng/L of CH3Hg A mean blank value greater than 0 045 ng/L CH_3Hg or a variability greater than 0 015 ng/L of CH_3Hg is unacceptable for low level ambient analysis

11 2 Sample Distillation

11 2 1 Weigh a 45-mL aliquot from a thoroughly shaken acidified sample into a 60-mL fluoropolymer distillation vial Add 200 µL of 1% APDC solution and replace the distillation cap, such that the tubing extends to the bottom of the vial

Note CAS experiments show that light reactive APDC degrades rapidly It is highly recommended that APDC be made fresh daily and stored in amber bottles

11 2 2 Repeat this procedure for all samples to be distilled in a set including three reagent water blanks and spiked samples

11 2 3 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples pour two additional 45-mL aliquots from a randomly selected sample Spike the aliquots at the level specified in Section 12 3 and process them in the same manner as the samples There should be two MS/MSD pairs for each analytical batch of 20 samples

11 2 4 For each sample prepare a 60-mL distillate receiving vial Add 5 0 mL reagent water to each receiving vial Cap so that the tubing extends into the water layer

UNCONTROLLED

11 2 5 Record the sample ID associated with each distillation and receiving vial It is important to develop an unambiguous tracking system such as the use of engraved vial numbers, because the distillation vials themselves cannot be labeled

11 2 6 Place each prepared distillation vial into one of the holes in the heating block and attach the fluoropolymer tubing to the incoming gas supply from the rotometer manifold Adjust the gas flow rate through the bubbler to 60 ± 20 mL/min (40 on the flow meter scale)

11 2 7 As each distillation vial with sample is placed into the heating block, attach the tubing from the receiving vessel to the inlet port of the distillation vessel Place the corresponding labeled distillation vial into the ice bath adjacent to the heating block

COPY

NOTE Be careful that the 5 mL water in the receiver vial does not freeze blocking the tubing from the distillation vial This can cause back flow and loss of sample To prevent this problem

1) Preheat the heating block to at least 100 °C before adding distillation vessels
2) Do not completely immerse the receivers in ice block for the first few minutes
3) Watch the receiver vessels carefully for the first 5 to 10 minute and check that
   a the flow meters maintain constant flow at 40 ± 3 on the rotometer
   b bubbles are visible in the receiver
   c warm fumes are distilling over
   d the receivers are not ice jammed

11 2 8 Once all the holes in a heating block are filled, place the aluminum lid over the vessel caps such that all tubing is passing without crimps through the slots and the lid is making metal-to-metal contact with the block (provides proper heating of the lid)

11 2 9 Turn on the temperature controllers to a pre-set block temperature of 125 ± 3 °C

11 2 10 Distill the samples until each receiving vial fills to the engraved 40 mL line This will take ~ 2 5 hr to 4 hr depending on temperatures gas flow rates and water

11 2 11 Different samples and locations on the block will distill at somewhat different rates so after about 2 hr, all of the tubes should be monitored frequently to avoid over-distillation As the individual samples fill to the line they should be removed

11 2 12 Over-distillation is the greatest potential risk for poor recoveries by this method If more than the prescribed amount of sample distills over, the risk of HCl fumes co-distilling increases Chloride and low pH interfere with the ethylation procedure

UNCONTROLLED

11 2 13 If any samples are suspected of over-distillation, they should be checked with pH paper If the distillate pH is less than 3 5, it should be discarded, rather than analyzed

11 2 14 Once all of the vials are distilled, the distillates may be stored at room temperature and in the dark for up to 48 h before analysis (loop the fluoropolymer tube around to close off the second port on the receiving vial) Don't refrigerate or store > 48 hr

11 2 15 The distillation-side (dirty) vials must be scrubbed thoroughly with a test-tube brush and alkaline detergent, then rinsed in reagent water to remove organics prior to acid cleaning Then the vials are filled with 10% HCl recapped with the tubing looped around to close off the port and placed in an oven at 80°C overnight

COPY

11 3 Ethylation Purge and Trap

11 3 1 If standards ethylation blanks or QCS are being analyzed pour 50 mL of reagent water into the bubbler add 0 3 mL of acetate buffer, the appropriate spike etc , and 0 05 mL 1% $NaBEt_4$ solution

11 3 2 Add the ~ 40 mL of distillate to a clean bubbler

11 3 3 Pipette 0 3 mL of acetate buffer to the bubbler

11 3 4 Pipette 0 050 mL of freshly thawed 1% $NaBEt_4$ solution Close the reaction vessel with the bubbler cap clip the cap on and swirl gently to mix

11 3 5 Allow the contents of the bubbler to react for 17 min The MMHg in the sample will be converted to volatile methylethyl mercury (MEHg)

11 3 6 After reaction, attach a Tenax ® trap to each bubbler with the 1/4 fluoropolymer fitting and purge the sample with Argon (~200 mL/min – 40 on the scale) for 17 min

11 3 7 The trap must be attached such that the gas from the bubbler enters the trap on side A (the crimped and numbered side of the trap)

11 3 8 Once the sample has been purged 17 min adsorbed water must be dried from the trap Switch the 4 way valve and purge argon through the trap only for 7 minutes to dry

11 3 9 After the 7 minute drying, remove the traps and plug the ends with Teflon plugs The sample is now ready for analysis Trapped MEHg is quantitatively stable for 6 hours

11 4 Thermal Desorption, GC-CVAFS analysis

UNCONTROLLED

11 4 1 Ensure the instrument is warmed up with the following conditions:

- Ar flow to GC is on at 10 psi and 30-35 on the flow meter
- GC oven is at 95 ^{0}C
- PMT voltage is typically 660 to 700 Volts Change this in order to achieve an offset as close to 50 000 counts as possible and very steady (± 15 counts)
- Pyrolytic and Trap Coil controllers are turned on
- Pyrolytic Coil is centered over glass wool in Pyrolytic Tube
- A daily Measure Instrument Noise test was done (typically 36-50)

COPY

11 4 2 Remove the previous trap from the GC

11 4 3 Attach next trap to the GC column using a 1/4" fluoropolymer friction fit connector such that side A (the crimped and numbered side) is facing toward the GC

11 4 4 Place the Nichrome wire heating coil around the trap centered over, and extending beyond the packing material on side A

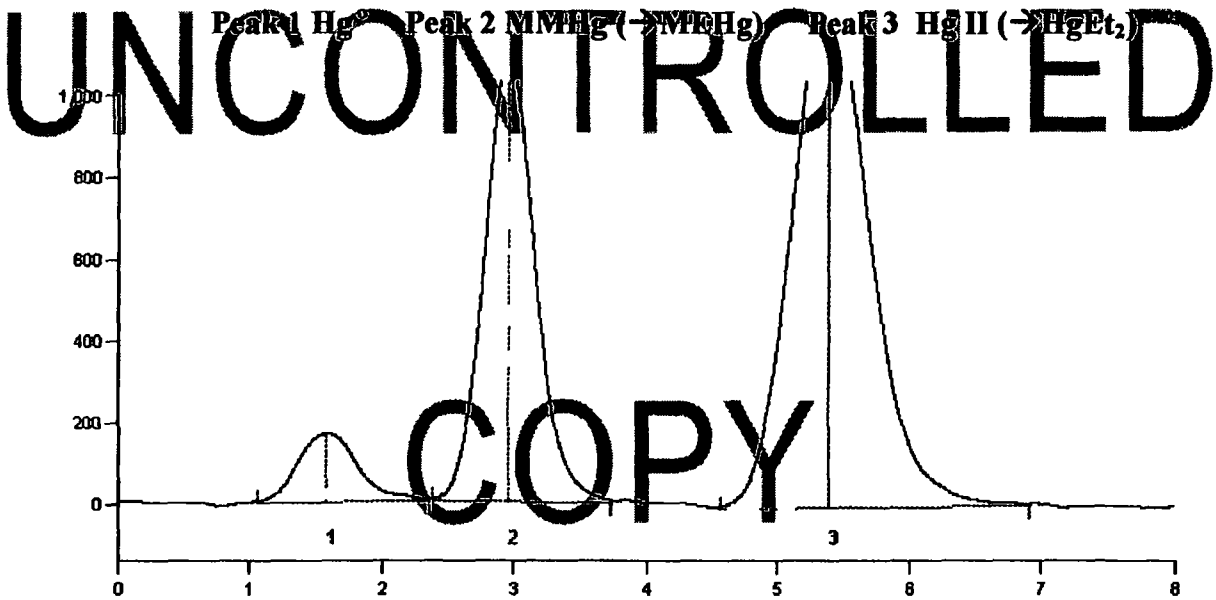
11 4 5 Re-connect the argon gas to side B of the trap

11 4 6 Allow at least 30 sec for the pressure in the system to equilibrate

11 4 7 Using the mercury Guru software apply power to the coil around the sample trap for 0 55-0 6 minutes (33-36 seconds using the software's automatic timer) to thermally desorb the ethylated mercury species from the sample trap into the GC column

11 4 8 Three peaks should emerge during the run The first peak (~1 5 min) is Hg ° which is residual, and non-quantitative The second peak to emerge (~3 min) is methylethyl mercury (the ethylation product of methylmercury) This is the peak of interest Following this (~5 min) is the peak for diethyl mercury ($(CH_3CH_2)_2Hg$) which is the ethylation product of Hg (II) If dimethyl mercury ($(CH_3)_2Hg$) were present in the sample it would appear as a second peak between Hg ° and methylethyl mercury-not fully resolved from the Hg ° See Representative Chromatogram below

Figure 2 A Representative Chromatogram for ~ 5 pg STD



UNCONTROLLED COPY

11 4 9 Allow the GC to run ~ 1 min beyond the point that the diethyl mercury (Hg(II)) peak returns to base line Place the next trap in line and proceed with next sample analysis

11 4 10 Peaks generated using this technique should be sharp and close to symmetrical (Unfortunately, some tailing is typical with this system) Methylethyl mercury elutes at approximately 2 5 min and has a width at half-height of ~ 20 sec Earlier peaks (Hg °, $(CH3)_2Hg$) are sharper while later peaks (diethyl mercury) are broader

11 4 11 If only the (Hg °) appears, it usually signifies that either that the pyrolytic column is not on or that $NaBEt_4$ was not added to the sample or sample leaked during trapping

11 4 12 Normally the Hg ° peak is small However some Hg ° is generated by thermal degradation of diethyl mercury during desorption So, when running samples with a high level of Hg (II), both the Hg ° and the diethyl mercury peaks will be bigger

11 4 13 The ratio of the two peaks is indicative of the quality of the Tenax ® trap As the trap degrades the amount of thermal breakdown of organo-mercurials increases Since the diethyl mercury is much more sensitive to thermal breakdown than the methyl-ethyl mercury, monitoring the latter peak can serve as an early warning for trap replacement Generally traps should be replaced any time the Hg ° peak grows to be as large as the diethyl mercury peak (Traps typically last 3 to 6 months)

11 5 Calibration and standardization

11 5 1 The calibration contains five or more non-zero points and the results of the analysis of at least one bubbler (ethylation) blanks

UNCONTROLLED

11 5 2 Using the procedure in Section 11.3 and 11.4, standards are analyzed by the addition of aliquots of Hg working standards A, B, or C (Section 8.14-8.16) directly into 50 mL of DIH_2O in the bubbler A typical curve might contain 2, 5, 10, 20 50, 100 pg for low end analysis, or for higher concentrations 5 50 100 500 1000 2000 pg

11 5 3 For each calibration point, subtract the mean peak area of the bubbler (ethylation) blank(s) for the batch from the area of each standard Calculate the calibration factors (CF) for Hg in each of the five to six standards as follows

COPY

Equation 1

$$CF = (R_S - R_{EB}) / C_S$$

where

R_S =Peak height or area of the standard
R_{EB} =Peak height or area of the ethylation blank
C_S =Concentration of the standard (ng/L)

Calculate the percent relative standard deviation (%RSD) of the individual calibration factors for all points on the curve

11 5 4 Calibration criteria are as follows

(a) There must be a minimum of five non zero calibration points
(b) The ethylation blank recovery of the low standard must be 65%-135%
(c) The %RSD for all Calibration Factors is ≤ 15%

11 5 5 Ongoing precision and recovery Perform the ongoing precision and recovery test to verify calibration prior to and at the end of each 20 field sample analytical batch

12 QA/QC REQUIREMENTS

12 1 Initial demonstration of laboratory performance

12 1 1 The analyst shall make an initial demonstration of ability to generate acceptable accuracy and precision the analyst shall perform the following initial precision and recovery (IPR) study

12 1 2 Analyze four replicates of the IPR solution (0 5 ng/L) according to the procedure beginning in Section 11

12 1 3 From the results of the four analyses, compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for CH_3Hg^+

UNCONTROLLED

12 1 4 Compare s and X with the corresponding limits for initial precision and recovery in Table 2 If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin If, however s exceeds the precision limit or X falls outside the acceptance range system performance is unacceptable Correct the problem and repeat the test

12 2 In recognition of advances that are occurring in analytical technology the analyst is permitted certain options to improve results or lower the cost of measurements These options include automation of the system, solvent extraction in place of distillation direct electronic data acquisition or changes in the detector (i e CVAAS AES, ICP/MS) Changes in the principle of the determinative technique such as the use of colorimetry are not allowed If an analytical technique other than the CVAFS technique specified in this method is used, that technique must have a specificity for CH_3Hg equal to or better than the specificity of the technique in this method

COPY

12 2 1 Each time this method is modified, the analyst is required to repeat the procedure in Section 12 1 If the change will affect the detection limit of the method the lab must demonstrate that the MDL (40 CFR Part 136 Appendix B) is lower than one-third the regulatory compliance level or lower than the MDL of this method whichever is higher If the change will affect calibration the analyst must recalibrate the instrument

12 2 2 The laboratory is required to maintain records of modifications made to this method These records include the following, at a minimum

12 2 2 1 The names titles addresses, and telephone numbers of the analyst(s) who performed the analyses and modification and the QC officer who witnessed and will verify the analyses and modification

12 2 2 2 A narrative stating the reason(s) for the modification(s)

12 2 2 3 Results from all quality control (QC) tests comparing the modified method to this method including the following

(a) Calibration
(b) Initial precision and recovery
(c) Matrix spike/matrix spike duplicate analysis
(d) Analysis of blanks
(e) Ongoing precision and recovery and quality control sample

12 2 2 4 Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result These data are to include the following

UNCONTROLLED

(a) Sample numbers and other identifiers
(b) Processing dates
(c) Analysis dates
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Copies of logbooks, chart recorder or other raw data output
(g) Calculations linking raw data to the results reported

12 3 Method Detection Limits and Method Reporting Limits

COPY

12 3 1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin To establish detection limits that are precise and accurate the analyst must perform the following procedure Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL Follow the analysis procedures in Section 11 to analyze the samples

12 3 2 Calculate the average concentration found (x) in µg/mL and the standard deviation of the concentrations (s) in µg/mL for each analyte Calculate the MDL for each analyte Refer to the CAS *SOP for The Determination of Method Detection Limits and Limits of Detection* (ADM-MDL) The MDL must be verified annually as described in the SOP ADM-MDL

12 3 3 The Method Reporting Limits (MRLs) used at CAS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors These MRLs are the levels to which CAS routinely reports results in order to minimize false positive or false negative results The MRL is normally two to ten times the method detection limit

12 3 4 Laboratory performance is compared to established performance criteria to determine whether the results of analyses meet the performance characteristics of the method

12 4 Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches In general, these include

12 4 1 The laboratory shall, on an ongoing basis demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control

UNCONTROLLED

12 4 2 The determination of CH_3Hg in water is controlled by an analytical batch An analytical batch is a set of samples distilled with the same batch of reagents and analyzed during the same 12-hour shift A batch may be from 1 to as many as 20 samples Each batch must be accompanied by at least three method blanks two OPR samples (at start and end of sequence), and a QCS In addition there must be one MS / MSD pair for every 10 samples (a frequency of 10%) The lab shall maintain records to define the quality of the data that are generated

12 4 3 MS / MSD samples are required to demonstrate accuracy and precision and to monitor matrix interferences Section 12 5 describes the procedure and spike criteria

COPY

12 4 4 Analyses of blanks are required to demonstrate acceptable levels of contamination Section 12 6 describes the procedures and criteria for analyzing blanks

12 5 Method accuracy—To assess the performance of the method on a given sample matrix the laboratory must perform either matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 10% of the samples from each site being monitored or at least one MS/MSD sample analysis for each sample set whichever is more frequent

12 5 1 The concentration of the CH_3Hg in the spiked sample shall be determined as follows

12 5 1 1 If, as in compliance monitoring, the concentration of CH_3Hg in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample whichever is greater

12 5 1 2 If the concentration of CH_3Hg in a sample is not being checked against a limit the spike shall be at 1-5 times the background concentration or at 1- 5 times the ML in Table 1, whichever is greater

12 5 2 Assessing spike recovery

12 5 2 1 Determine the background concentration (B) by analyzing one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11 If the expected background concentration is known from previous experience or other knowledge the spiking level may be established a priori

12 5 2 2 Prepare a spiking solution to produce an appropriate level in the sample

12 5 2 3 Spike two sample aliquots with the spiking solution and analyze these aliquots as described in Section 11 to determine the concentration after spiking (A)

UNCONTROLLED

12 5 2 4 Calculate the percent recovery (P) in each aliquot using Equation 2

Equation 2

$$P = 100 * (A - B) / T$$

Where

A=Measured concentration of analyte after spiking
B=Measured concentration of analyte before spiking
P=Percent recovery
T=True concentration of the spike

COPY

12 5 3 Compare the percent recovery (P) with the QC acceptance criteria in Table 2

12 5 3 1 If P falls outside the range for recovery in Table 2, the CH_3Hg analysis has failed to meet the established performance criteria If P is unacceptable analyze the OPR standard If the OPR is within established performance criteria (Table 2) the analytical system is within specification and the problem can be attributed to interference by the sample matrix

12 5 3 2 If the interference can be attributed to sampling the site or discharge should be re-sampled If the interference can be attributed to a method deficiency, the analyst must modify the method, repeat the test required in Section 12 1 2 and repeat analysis of the sample and MS/MSD However when this method was written, there were no known interferences in the determination of CH_3Hg using this method If such a result occurs the lab must thoroughly investigate

12 5 3 3 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits The analyst must identify and correct the problem and reanalyze the sample batch

12 5 4 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 3 using the CH_3Hg concentrations found in the MS and MSD Do not use the recoveries calculated in Section 12 5 2 4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration

UNCONTROLLED

Equation 3

$$RPD = 200 * |D1 - D2| / D1 + D2$$

Where

RPD = Relative percent difference
D1 = Concentration of CH_3Hg in the MS sample
D2 = Concentration of CH_3Hg in the MSD sample

12 5 5 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2 If the criterion is not met the system performance is unacceptable The problem must immediately be identified and corrected and the analytical batch reanalyzed

COPY

12 5 6 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records maintained After analyzing five samples in which the recovery passes, compute the average percent recovery (Pa) and the standard deviation of the percent recovery (sp) Express the accuracy assessment as a percent recovery interval from Pa - 2sp to Pa + 2sp For example if Pa = 90% and sp = 10% for five analyses the accuracy interval is expressed as 70-110% Update the accuracy assessment regularly (e g , after every five to ten new accuracy measurements)

12 6 Blanks—Blanks are critical to the reliable determination of CH_3Hg at low levels The sections below give the minimum requirements for analysis of blanks

12 6 1 Ethylation blanks—Reagent water typically contains no CH_3Hg The reagent (ethylation) blank may conveniently be determined by adding 0 3 mL of acetate buffer and 0 050 mL of 1% NaBEt4 solution to 50 mL of reagent water in the reaction vessel NOTE Never use a previously ethylated water sample as a build-up of triethyl boron gas occurs yielding negative interference and poor chromatography

12 6 1 1 A single ethylation blank is analyzed with each analytical run as part of the calibration sequence This value is used to blank correct the standard curve

12 6 1 2 The presence of more than 2 pg of CH_3Hg indicates a problem with the reagent water or one of the reagent solutions An investigation of the cause of the high blank can be made by varying, one at a time the amounts of buffer, reagent water and NaBEt4 Because NaBEt4 cannot be purified a new batch should be made from different reagents and should be tested for Hg levels if the level of CH_3Hg is too high If the reagent water is found high, this can be remedied by replacing the purification cartridges

12 6 2 Method blanks

UNCONTROLLED

12 6 2 1 The method blanks (distillation blanks) are prepared by the distillation and analysis of 45 mL aliquots of 0.4% HCl acidified reagent water, exactly as if they were samples

12 6 2 2 Three method blanks should accompany each analytical batch The mean blank value should be less than 0 045 ng/L of CH_3Hg, and the variability should be less than 0 015 ng/L of CH_3Hg or else the system is unacceptable for low level ambient analysis

12 6 3 Field blanks

COPY

12 6 3 1 Analyze the field blank(s) shipped with each sample set Analyze the blank immediately before analyzing the samples in the batch

12 6 3 2 If CH_3Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1) or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes

12 6 3 3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blanks, the average concentration plus 2 STD DEV must be less than the regulatory compliance level or less than 1/2 the level in the associated sample whichever is greater

12 6 3 4 If contamination of the field blank(s) and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event

12 6 4 Equipment blanks—Before any sampling equipment is used at a given site the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that sampling equipment is free from contamination Two types of equipment blanks are required bottle blanks and sampler check blanks

12 6 4 1 Bottle blanks—After undergoing the cleaning procedures in this method bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures A representative set of sample bottles should be filled with reagent water acidified to 0 4 - 0 5% HCL and allowed to stand for a minimum of 24 hr then analyzed for contamination If any bottle shows signs of contamination, the problem must be identified the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again

UNCONTROLLED

12 6 4 2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method) Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed

12 6 4 2 1 Sampler check blanks are generated by filling a large carboy or other container with reagent water and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method) For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle and capping Subsurface sampler check blanks are collected by immersing the submersible pump or intake tubing into the water and pumping water into a sample container

COPY

12 6 4 2 2 The sampler check blank must be analyzed using the procedures in this method If CH_3Hg or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected Equipment must be demonstrated to be free from CH_3Hg and interferences before the equipment may be used in the field

12 6 4 2 3 Sampler check blanks must be run on all equipment that will be used in the field If for example samples are to be collected using both a grab sampling device and a subsurface sampling device a sampler check blank must be run on both pieces of equipment

12 7 Ongoing precision and recovery (OPR)—To demonstrate that the analysis system is within specified limits and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations

12 7 1 Analyze the OPR solution (0 5 ng/L) prior to the analysis of each analytical batch according to the procedure in Section 11 An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift Subtract the peak height (or peak area) of the ethlyation blank from the peak height (or area) for the OPR and compute the concentration for the ethylation blank-subtracted OPR

12 7 2 Compare the OPR with the limits in Table 2 If the concentration is within the spec range, analysis of samples and blanks may proceed If the concentration is outside the specified range, the analytical process is not within the specified limits Correct the problem and repeat the OPR test

UNCONTROLLED

12 7 3 The lab should add results that pass the specification to IPR and previous OPR data and update QC charts to form a graphic representation of lab performance The laboratory should also develop a statement of laboratory data quality by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr) Express the accuracy as a recovery interval from R - 2sr to R + 2sr For example, if R = 95% and sr = 5%, the accuracy is 85- 105%

12 8 Quality control sample (QCS)—The laboratory must obtain a QCS from a source different from the CH_3Hg used to produce the standards used routinely in this method The QCS should be analyzed as an independent check of instrument calibration in the middle of the analytical batch (e g , for a batch of 14 samples, the QCS is analyzed after the 7th sample)

COPY

12 9 Depending on specific program requirements the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling sample transportation, and storage techniques The relative percent difference (RPD) between field duplicates should be less than 35% If the RPD of the field duplicates exceeds 35% the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event

13 DATA REDUCTION, REVIEW, AND REPORTING

13 1 Calculate the following parameters for each analytical batch

13 1 1 Ethylation blank (n = 1) or the mean ethylation blank (n > 1)

13 1 2 Ethylation-blank subtracted calibration factor for each standard (Cf_x Section 11 5 3) and peak measurement for each sample (R_s)

13 1 3 The mean calibration factor (Cf_m), standard deviation of the calibration factor (SD) and relative standard deviation (RSD) of the calibration factor

UNCONTROLLED

13 2 Compute the concentration of CH_3Hg in ng/L (parts-per-trillion, ppt) according to Equation 4

Equation 4

$$[CH_3Hg](ng/L) = (R_S - R_{EB}) / CF_m * V$$

Where
R_s = peak height (or area) of signal for CH_3Hg in sample
R_{EB} = peak height (or area) of signal for CH_3Hg in ethylation blank (n = 1) or mean ethylation blank (n > 1)
CF_m = mean calibration factor
V = Sample volume (L)

COPY

13 3 The CH_3Hg concentration of the mean method blank is subtracted from the sample concentration calculated above to obtain the **net** in situ CH_3Hg concentration (Equation 5)

Equation 5

$$[CH_3Hg]_{net} = [CH_3Hg]_{Sample} - [CH_3Hg]_{MB}$$

where

$[CH3Hg]_{net}$ = net in situ CH_3Hg concentration (ng/L)
$[CH3Hg]_{sample}$ = ethylation-blank corrected concentration of CH_3Hg in the sample (ng/L Equation 4)
$[CH3Hg]_{MB}$ = concentration of CH_3Hg in the mean method blank (ng/L Equation 4)

13 4 Reporting

13 4 1 All results are reported after subtraction of mean method blanks (Equation 5)

13 4 2 Under the conditions described here, the distillation procedure is not 100% efficient in recovering CH_3Hg because not all of the sample volume can be distilled to avoid co-distillation of HCl Laboratories should calculate the efficiency of the distillation for their laboratory This calculation is done by keeping a running mean of the last 30 recoveries calculated for precision and recovery samples (IPR and OPR) excluding all values that are more than two standard deviations from the mean Since the distillation technique is inherently and reproducibly non-quantitative all results should be recovery corrected by an empirically derived factor (Equation 6)

UNCONTROLLED

Equation 6

$$F = 100 / R$$

where F = Empirically derived correction factor
R = Recovery (the running mean of the last 30 IPR and OPR samples)

13 4 3 Report all values in ng/L to three significant figures Report results below the MRL as <0 1 ng/L, or as required by the permitting authority or in the permit

COPY

13 5 It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run Results for QC analyses are calculated and recorded as specified in section 12

13 6 If any sample result is over the calibration range prepare and analyze a diluted sample using the appropriate dilution factor to bring within range

The data packet for the sequence is submitted for review by supervisor or designee

13 7 Refer to the SOP *Laboratory Data Review Process* (ADM-DREV) for instructions for data review

14 METHOD PERFORMANCE

14 1 This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

14 2 The method detection limit (MDL) is established using the procedure described in the SOP for *The Determination of Method Detection Limits and Limits of Detection* (ADM-MDL) Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual

15 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also refer to the *SOP for Nonconformity and Corrective Action* for procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the *SOP for Report Generation* or in project-specific needs

16 POLLUTION PREVENTION

UNCONTROLLED

It is the laboratory's practice to minimize the amount of solvents acids and reagent used to perform this method wherever feasible Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site Environmental threat from solvent and reagent use in this method, can be minimized when recycled or disposed of properly

17 WASTE MANAGEMENT

17 1 The laboratory will comply with all Federal State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual

COPY

17 2 This method uses acid Waste acid is hazardous to the sewer system and to the environment All acid waste must be neutralized to a pH of 2 5-12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record See the CAS EH&S Manual for details

18 TRAINING

18 1 Refer to the *SOP for Documentation of Training* (ADM-TRANDOC) for standard procedures

18 2 Training outline

18 2 1 Review literature (see references section) Read and understand the SOP Also review the applicable MSDS for all reagents and standards used Following these reviews, observe the procedure as performed by an experienced analyst at least three times

18 2 2 The next training step is to assist in the procedure under the guidance of an experienced analyst During this period the analyst is expected to transition from a role of assisting to performing the procedure with minimal oversight from an experienced analyst

18 2 3 Perform initial precision and recovery (IPR) study as described above Summaries of the IPR are reviewed and signed by the supervisor Copies may be forwarded to the employee's training file

18 2 4 For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability

18 3 Training is documented following the SOP for Documentation of Training

NOTE When the analyst training is documented by the supervisor on internal training documentation forms the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently

19 CHANGES SINCE THE LAST REVISION

UNCONTROLLED

19 1 Section 12 3 2 removed annual MDL requirement and referenced ADM-MDL SOP for (LOD) verification procedure

19 2 Removed footnotes from table 2.

20 REFERENCES

EPA Method 1630 Methyl Mercury in Water by Distillation, Aqueous Ethylation Purge and Trap and CVAFS January 2001

COPY

Table 1 Methyl Mercury Analysis Using Method 1630
Lowest Water Quality Criterion, Method Detection Limit, and Minimum Level

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Methyl Mercury (CH_3Hg)	None	0 02 ng/L	0 06 ng/L

UNCONTROLLED

NOTES

1 Lowest of the freshwater, marine, and human health ambient water quality criteria promulgated by EPA for 9 States and the District of Columbia at 40 CFR Part 131 on May 4 1995 (60 FR 22229)

2 Method Detection Limit as determined by the procedure in 40 CFR Part 136 Appendix B

3 Minimum Level (ML)

COPY

Table 2 Quality Control Acceptance Criteria for Performance Tests In EPA Method 1630

Metal	IPR		OPR	Method Blanks		MS/MSD	
	S	X		Max	Mean	% R	RPD
Methyl Mercury (CH_3Hg)	31%	69-131%	67-133%	< 0 1 ng/L	< 0 05 ng/L	65-135%	35%

STANDARD OPERATING PROCEDURE

NITRATE/NITRITE, NITRITE BY FLOW INJECTION ANALYSIS
GEN-353 2
Revision 6
January 5, 2006

UNCONTROLLED

Approved By _____ Supervisor 1/19/06 Date

_____ QA Manager 1-19-06 Date

_____ Laboratory Manager 1/19/06 Date

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2006

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

NITRATE/NITRITE, NITRITE BY FLOW INJECTION ANALYSIS

1 SCOPE AND APPLICATION

The purpose of this procedure is to determine the concentration of Nitrite, or Nitrate/Nitrite in water and wastewater samples using EPA Method 353 2 This procedure is applicable to determination of Nitrite or Nitrate/Nitrite concentrations greater than 0 02 mg/L in water and wastewater The Method Reporting Limits (MRLs) and Method Detection Limits (MDLs) are listed in Table 1

UNCONTROLLED

2 METHOD SUMMARY

2 1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite The nitrite is then determined by diazotization with sulfanilamide, and coupling with N-(1-napthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically Separate, rather than combined nitrate/nitrite, values are obtained by carrying out the procedure first with, and then without the Cd reduction column, and subtracting NO_2 from NO_3/NO_2 to obtain NO_3

COPY

2 2 Soil samples may be analyzed following an extraction and filtration procedure

3 DEFINITIONS

3 1 Analysis Sequence - Samples are analyzed in a set referred to as an analysis sequence The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation

3 2 Independent Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration The ICV standards are prepared from a materials obtained from a source different from that used to prepare calibration standards

3 3 Laboratory Control Sample (LCS) - A blank sample fortified with a known amount of target analyte and taken through the entire analysis process The LCS is used to assess the accuracy of the analysis process

3 4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis Samples are split into duplicates, spiked, and analyzed as a MS/DMS pair Percent recoveries are calculated for each of the analytes detected The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision

3 5 Standard Curve - A standard curve is a calibration curve which plots concentrations of a known analyte standard versus the instrument response to the analyte A calibration is performed using the range for which the intrument response is linear and uses a linear calibration model The appropriate criteria for assessing the validity of the calibration curve must be followed prior to quantitation of target analytes in actual sample analyses

UNCONTROLLED

3 6 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process The method blank is carried through the entire analytical procedure

3 7 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals Used to verify that the initial calibration curve is still valid for quantitative purposes

COPY

3 8 Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses

4 INTERFERENCES

4 1 Suspended solids can clog the reduction column and restrict sample flow Since nitrate/nitrite is found in a dissolved state the sample may be filtered before analysis

4 2 Dissolved metals may cause low results EDTA can be added to the samples to eliminate this interference Also, 10N NaOH can be added to the samples to precipitate the metals and eliminate this interference

4 3 The buffer in this method allows analysis of sulfuric acid-preserved samples without pH adjustment Negative peaks during flow injection analysis, or peaks which split into

groups, are an indication that samples have been excessively acidified, and must be adjusted to a pH between 5 0 and 8 0 with 10 N NaOH or NH_4OH prior to analysis

4 4 Samples which contain large amounts of oil and grease will coat the surface of the cadmium The sample may be pre-extracted with an organic solvent to alleviate this interference

4 5 Highly colored samples may require background correction To perform a background correction, run the samples through the flow injection analyses without the sulfanilamide reagent Run buffer through the sulfanilamide line in place of the color reagent

UNCONTROLLED

5 SAFETY

5 1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves

5 2 Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method

COPY

5 3 Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard Use nitrile or latex gloves while handling pellets or preparing solutions

5 4 Be cautious of fumes when preparing the NH_4Cl buffer

5 5 Dispose of culture tubes in the broken glass container

5 6 Empty waste containers in the hood

6 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

Samples collected in white plastic bottles are unpreserved Samples collected in yellow label plastic bottles are preserved If nitrate and nitrite are to be determined separately, the sample should be stored at 4°C or below, and analyzed within 48 hours If combined nitrate/nitrite is to be determined, the sample should be preserved with H_2SO_4 to a pH of 2 or less and stored at 4 ± 2°C for 28 days or less

7 APPARATUS AND EQUIPMENT

7 1 Lachat QuikChem AE Flow Injection Analyzer and Data System

7 2 Bran & Luebbe AA3 Flow Injection Analyzer and Data System

7 3 Copper-Cadmium Reduction Column - Lachat Part #50237 For Bran & Luebbe, Irama Part # 165-0301-01

7 4 Standard Laboratory Glassware and digital pipettors for preparing reagents and dilutions

7 5 Wrist action shaker

8 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

UNCONTROLLED

8 1 10N NaOH , Add 100 g NaOH to 250 ml DI water very slowly, and swirl to dissolve (reaction is highly exothermic)

8 2 Ammonium Chloride Buffer (Lachcat) Dissolve 85 0 g NH_4Cl and 1 0 g Na_2EDTA 2 H_2O in DI water, and dilute to approximately 800 ml Adjust the pH to 8 5 with 30% NH_4OH, dilute to 1,000 ml with DI water, and mix by inversion

8 3 Ammonium Chloride Buffer (Bran & Luebbe) Dissolve 97 0 g NH_4Cl and 0 1 g Na_2EDTA 2 H_2O in DI water, and dilute to approximately 900 ml Add 1 0mL stock copper sulfate and mix Dilute to 1,000 ml with DI water, adjust to a pH of 8 5 with 50% NaOH, and add 2 0mL Brij-35

COPY

8 4 Sulfanilamide Color Reagent (Lachat) Add 600 ml of DI water and 100 ml phosphoric acid to a 1 l flask Then add 40 0 g sulfanilamide and 2 0 g N-(1-naphthyl) ethylene diamine dihydrochloride to the flask, and shake to wet Mix with a magnetic stirrer until all dry chemical is dissolved (approximately 30 minutes), remove the stir bar, and dilute to the mark with DI water Store the reagent in a labeled brown glass bottle for no more than one month

8 5 Sulfanilamide Color Reagent (Bran & Luebbe) Add 800 ml of DI water and 185 ml phosphoric acid to a 1 liter flask Then add 9 1 sulfanilamide and 0 71 g N-(1-naphthyl) ethylene diamine dihydrochloride to the flask, and shake to wet Mix with a magnetic stirrer until all dry chemical is dissolved (approximately 30 minutes), remove the stir bar, and dilute to the mark with DI water and add 1 mL Brij-35 Store the reagent in a labeled brown glass bottle for no more than one month

8 6 Copper Sulfate Stock Solution Dissolve 2 5g copper sulfate in 600mL DIW Dilute to one liter and mix thoroughly

8 7 Nitrate Stock Solution In a 100 mL flask, dissolve 6 068g dried $NaNO_3$ to 100ml final volume with DIW Concentration = 10 000 ppm It is standard practice to use the Ion Chromotography Stock

8 8 Nitrite Stock Solution In a 250 mL flask, dissolve 12 316 g dried $NaNO_2$ to 250ml final volume with DIW Concentration = 10,000 ppm It is standard practice to use the Ion Chromotography Stock

8 9 Working Nitrate Solution Dilute 1 0 ml of Stock Nitrate Solution to 100 ml with DI water 1 ml = 100 μg NO_3-N Prepare fresh weekly

UNCONTROLLED

8 10 Working Nitrite Solution Dilute 1.0 ml of Stock Nitrite Solution to 100 ml with DI water 1 ml = 100 μg NO_2-N Prepare fresh weekly

8 11 Calibration Standards Prepare a series of standards according to one of the options in Table 2 All standards are prepared with DI water, with the exception that standards must be prepared in substitute ocean water (see EPA 353 2) if saline waters are to be analyzed

8 12 KCl, 2M, dissolve 150g of KCl in 1L deionized water

COPY

9 PREVENTIVE MAINTENANCE

9 1 No specific maintenance steps are needed other than normal cleaning and inspection of apparatus

9 2 Change reagent and sampling lines when they are flat

9 3 For problems encountered with Lachat operation, see Lachat troubleshooting guide

9 4 For problems encountered with Bran & Luebbe, see Bran & Luebbe troubleshooting guide

10 RESPONSIBILITIES

10 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

10 2 It is the responsibility of the department supervisor/manager to document analyst training Documenting method proficiency is also the responsibility of the department supervisor/manager

11 PROCEDURE

11 1 Sample preparation

11 1 1 Water samples do not require a preparation step Filtering is included in analysis procedures below

UNCONTROLLED

11 1 2 For soil sample extraction perform the following steps

11 1 2 1 Weigh out 10 g of sample into a 50 mL centrifuge tube

11 1 2 2 Spike appropriate QC sample with 0 5 mL of 10 000 ppm NO_3 stock solution

11 1 2 3 Bring to 50mL volume with 2M KCl The Method blank contains only KCl

11 1 2 4 Shake samples for 30 minutes on the wrist-action shaker

COPY

11 1 2 5 Centrifuge samples for 10-20 minutes

11 1 2 6 Filter supernatant with 0 45µm filter Samples are now ready for analysis

11 2 Procedure for Lachat QUIKCHEM AE Analyzer

11 2 1 Turn both the Lachat and computer on Let warm up for ~ 20 minutes

11 2 2 Degas carrier and buffer with helium for 5 minutes

11 2 3 Load method and set up instrument according to Lachat QuikChem AE method

11 2 4 Fasten reagent lines across the pump and into the reagent bottles Start pump

11 2 5 Calibrate with nitrate standards appropriate to the expected NO_3/NO_2 levels in the sample

11 2 6 Connect cadmium column at the 2nd valve so the sample runs through the column before coloring For $NO_3 \rightarrow NO_2$ reduction

11 2 7 For NO_2 determination calibrate with NO_2 standards

11 2 8 Filter samples through a 0 45 μ syringe type membrane filter into auto sampler vials, and arrange the run according to Table 2 If the initial sample analysis results in a negative peak, due to dissolved metals interference, add 10N NaOH dropwise until the precipate drops out of solution Centrifuge the sample and analyze

UNCONTROLLED

11.2 9 Start calibration and sample tray after reagents flow through the flow cell and a steady baseline appears. Refer to Table 3 for a typical run sequence

11 2 10 CCV (Continuing Calibration Verification) - A CCV must be analyzed following every tenth vial on the autosampler The CCV is a 3 0 mg/L NO_3-N standard and recovery must be between 2 7 and 3 3 mg/L The CCV for NO_2-N only is a 3 0 mg/L NO_2 standard

11 2 11 CCB (Continuing Calibration Blank) - A CCB must be analyzed following every CCV The CCB is a portion of DI water, and the result must be below the MRL

COPY

11 2 12 Cleanup - Run 1N HCl through board lines followed by DI water, then NH_4Cl buffer Remove the cadmium column Again pump 1N HCl across the board lines followed by DI water Pump air through the lines to dry

11 3 Procedure for Bran & Luebbe Analyzer

11 3 1 Turn on the auto sampler, the pump, the digital colorimeter, then the computer

11 3 2 Load method and set up instrument according to Bran & Luebbe method

11 3 3 Fasten correct reagent lines and pump carrier until a stable baseline is achieved Place lines into appropriate reagents and pump until a stable baseline is achieved

11 3 4 After a stable baseline is achieved, turn off the pump and switch valve to flow through the cadmium columns (for $NO_3 \rightarrow NO_2$ reduction), turn pump back on and pump until a stable baseline is achieved again

11 3 5 Calibrate with nitrate standards appropriate to the expected NO_3/NO_2 levels in the sample

11 3 6 For NO_2 determination calibrate with NO_2 standards

11 3 7 Filter samples through a 0 45 μ syringe type membrane filter into auto sampler vials, and arrange the run according to Table 3 If the initial sample analysis results in a negative peak, due to dissolved metals interference, add 10N NaOH dropwise until the precipate drops out of solution Centrifuge the sample decant supernate, and adjust pH to between 5 and 8 with 5N H_2SO_4, then analyze as normal

11 3 8 Start calibration and sample tray after reagents flow through the flow cell and a steady baseline appears Refer to Table 3 for a typical run sequence

UNCONTROLLED

11 3 9 CCV (Continuing Calibration Verification) - A CCV must be analyzed following every tenth vial on the auto sampler The CCV is a 2.0 mg/L NO_3-N standard, and recovery must be within 10 percent of expected value The CCV for NO_2-N only is a 2 0 mg/L NO_2 standard

11 3 10 CCB (Continuing Calibration Blank) - A CCB must be analyzed following every CCV The CCB is a portion of DI water, and the result must be below the MRL

11 3 11 Cleanup - Run 1N HCl through board lines followed by DI water If the cadmium column valve is open (NO_3/NO_2 analysis), stop the pump, switch valve off, then start the pump again The cadmium column should be filled with DI water for storage Remove reagent lines from the DI water and pump the lines dry

COPY

12 QA/QC REQUIREMENTS

12 1 Initial Precision and Recovery Validation - The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made To do this, four LCS aliquots are prepared and analyzed The average percent recovery must be 90-110% and the RSD < 30%

12 2 A method detection limit (MDL) study must be undertaken before analysis of samples can begin To establish detection limits that are precise and accurate, the analyst must perform the following procedure Spike a minimum of seven blank replicates at a level near or below the MRL Follow the procedures starting in Section 11 to analyze the samples Refer to the CAS SOP for The Determination of Method Detection Limits and Limits of Detection

12 3 Linear Calibration Range - The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument

response is observed or expected The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument The verification of linearity must use a minimum of a blank and three standards If any verification data exceeds the initial values by ±10% linearity must be reestablished If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion

12 4 Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches In general, these include

UNCONTROLLED

12 4 1 ICV - A 3.0 mg/L NO_2 for Lachat, and 2 0 mg/L NO_2 for Bran & Luebbe standard is analyzed with every calibration to check the efficiency of the reduction column Recovery must be within 10% of the true value

12 4 2 LCS - A Laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples Result must be within 90-110% of the true value Calculate the LCS recovery as follows

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

COPY

12 4 3 Method Blank - A method blank (Deionized Water) must be filtered and analyzed with each batch of 20 or fewer samples The result must be below the MRL

12 4 4 Sample Duplicates - One sample per batch of 20 or fewer samples must be analyzed in duplicate Relative Percent Difference must be $\leq$ 20%

Calculate Relative Percent Difference (RPD) as

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1 = result for the sample
R2 = result for the sample duplicate

12 4 5 Matrix Spikes One spike sample must be analyzed with each batch of 20 or fewer samples Recovery must be in the range of 90-110% Calculate percent recovery (%R) as

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

13 DATA REDUCTION, REVIEW, AND REPORTING

UNCONTROLLED

13 1 Calculations

13 1 1 For water samples, the instrument will readout the sample concentration values No additional calculations are needed other than taking into account any dilutions made

13 1 2 For soil samples, the instrument will readout the analyzed sample concentration These are used to calculate the soil sample concentration, taking into account the initial weight, final volume, and any dilutions made

13 2 Data Reporting

COPY

13 2 1 Report results as follows

- For Nitrate/Nitrite as "Nitrate/Nitrite as Nitrogen" in mg/L units
- Report results for Nitrite as "Nitrite as Nitrogen" in mg/L units
- Report results for Nitrate as "Nitrate as Nitrogen" in mg/L units
- Soil samples should be reported as method 353 2 Modified in mg/kg (dry wt basis)

13 2 2 Report results to 3 significant figures unless the sample was diluted If a dilution was performed, report 2 significant figures

13 3 It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run Results for QC analyses are calculated and recorded as specified in section 11 of SOP Average, RPD, spike level and spike recovery are entered on the analytical spreadsheet for corresponding samples All data will be initialed, dated and attached to required data quality worksheet

13 4 The data packet for the sequence is submitted for review by supervisor or designee The results are transferred to the appropriate report form located in the CAS network

directory R \WET\WIP These forms are made from templates located in R \WET\FORMS

13 5 Refer to the SOP for *Laboratory Data Review Process* for general instructions for data review

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements

UNCONTROLLED COPY

15 METHOD PERFORMANCE

15 1 This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

15 2 The method detection limit (MDL) is established using the procedure described in the SOP for *The Determination of Method Detection Limits* (ADM-MDL) Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual

16 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly

17 WASTE MANAGEMENT

17 1 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual

17 2 This method uses a base Waste base is hazardous to the sewer system and to the environment All waste must be neutralized to a pH of 2 5 12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be

documented on the treatment by generator record See the CAS EH&S Manual for details

18 TRAINING OUTLINE

18 1 Review literature (see references section) Review the SOP Also review the applicable MSDS for all reagents and standards used Following these reviews, observe the procedure as performed by an experienced analyst at least three times

18 2 The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of approximately two weeks During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst

UNCONTROLLED

18 3 Perform initial precision and recovery (IPR) study as described above for water samples Summaries of the IPR are reviewed and signed by the supervisor Copies may be forwarded to the employee's training file

19 REFERENCES

19 1 *Standard Methods for the Examination of Water and Wastewater* 18th Ed , 1992

19 2 USEPA, *Methods for Chemical Analyses of Water and Wastes* EPA-600/4-79-020 March 1983 - Method 353 2

19 3 Lachat QuikChem Methods

19 4 Bran & Luebbe Methods

COPY

TABLE 1

Target Analytes, MRLs, and MDLs (Lachat)

Analyte	Method Detection Limit	Method Reporting Limit
Nitrate/Nitrite-N	0 03 mg/L	0 2 mg/L
Nitrate-N	0 03 mg/L	0 2 mg/L
Nitrite-N	0 02 mg/L	0 2 mg/L

UNCONTROLLED

Target Analytes, MRLs, and MDLs (Bran & Luebbe)

Analyte	Method Detection Limit	Method Reporting Limit
Nitrate/Nitrite-N	0 003 mg/L	0 05 mg/L
Nitrate-N	0 003 mg/L	0 05 mg/L
Nitrite-N	0 002 mg/L	0 05 mg/L

COPY

TABLE 2
Calibration Standards Preparation
Lachat

Routine Calibration Standards

Volume of 100 µg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0	100	0 00
0 10	100	0 10
0 20	100	0 20
1 00	100	1 00
3 00	100	3 00
5 00	100	5 00
7 00	100	7 00

UNCONTROLLED

Low Level Calibration Standards

Volume of 10 µg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (µg/L)
0	100	0 00
0 2	100	20 0
0 5	100	50 0
0 7	100	70 0
1 0	100	100 0
1 5	100	150 0
2 0	100	200 0

COPY

TABLE 3
Calibration Standards Preparation
Bran & Luebbe

Routine Calibration Standards

Volume of 100 μg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0 00	100	0 00
0 05	100	0 05
0 50	100	0 50
2 00	100	2 00
4 00	100	4 00

UNCONTROLLED COPY

TABLE 4
Analytical Run Scheme
Lachat

Step	Sample
1	ICB
2	ICV (3 0 mg/L NO_2 Std)
3	CCV 1
4	CCB 1
5	LCS
6	Method Blank
7	Sample
8	Sample Dup
9	Sample Spike
10	Sample
11	Sample
12	Sample
13	Sample
14	Sample
15	CCV 2
16	CCB 2
17 26	10 more Samples
27	CCV 3
28	CCB 3

Repeat steps 5-28 for remainder of samples

UNCONTROLLED COPY

TABLE 5
Analytical Run Scheme
Bran & Luebbe

Step	Sample
1	ICV (2 0 mg/L NO_2 Std)
2	ICB
3	CCB-1
4	CCV 1
5	LCS
6	Method Blank
7	Sample
8	Sample Dup
9	Sample Spike
10	Sample
11	Sample
12	Sample
13	Sample
14	Sample
15	CCB 2
16	CCV 2
17 26	10 more Samples
27	CCB-3
28	CCV 3

Repeat steps 5-28 for remainder of samples

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

AMMONIA BY FLOW INJECTION ANALYSIS

SOP No GEN-350 1

UNCONTROLLED

Revision 7

May 1, 2007

Approved by _____ Supervisor _____ Date 5/1/07

_____ QA Manager _____ Date 5-1-07

_____ Laboratory Manager _____ Date 5/1/07

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso Washington 98626

© Columbia Analytical Services, Inc 2007

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

AMMONIA BY FLOW INJECTION ANALYSIS

1 SCOPE AND APPLICATION

1 1 This procedure is used to determine the concentration of Ammonia in aqueous samples including water, wastewater, and groundwater using EPA Method 350 1 and Standard Methods 4500 NH_3 G Ammonia in soil samples can be determined following extraction in a potassium chloride solution

UNCONTROLLED

1 2 This method is applicable for the determination of ammonia concentrations in a range of 0 02 mg/L to 4 0 mg/L The MRL for this test is 0 05 mg/L and the MDL as been determined at 0 006 mg/L

2 METHOD SUMMARY

2 1 For EPA 350 1, water samples are distilled into a solution of boric acid or 0 04N sulfuric acid, using the procedure described in and 350 2 and SM 4500 NH_3 B Standard Methods 4500 NH_3 G may be performed with or without sample distillation

2 2 Soil and sediment samples are extracted with 2M KCL using a wrist action shaker and extracts analyzed using the water procedure (based on the Plumb extraction procedure)

COPY

2 3 Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity The absorbance of the reaction product is measured at 660 nm, and is directly proportional to the original ammonia concentration in the sample

3 DEFINITIONS

3 1 Stock standard solution - a concentrated solution containing a single certified standard that is a method analyte Stock solutions are used to prepare calibration standards

3 2 Calibration standards - a solution of analytes prepared in the laboratory from stock standard solutions, diluted as needed, and used to calibrate the instrument response with respect to analytical concentration

3 3 Laboratory Control Standards (LCS) - a solution of analytes prepared in the laboratory from stock standard solutions purchased or prepared independently from calibration standards

3 4 Method Blank (MB) - a solution of the laboratory prepared deionized water that is carried through analysis like a sample to serve as a measure of contamination associated with laboratory storage, preparation, or instrumentation

3 5 Continuing calibration verification standard (CCV) a solution of analytes prepared in the laboratory from stock standards to be at approximately the midpoint of calibration curves CCV's are analyzed every 10 injections to verify that the instrument system performance has not changed during the course of the analytical run

3 6 Continuing calibration blank (CCB) - a blank solution of deionized water CCB's are analyzed every 10 injections to verify that the instrument system has not become contaminated during the course of the analytical run

UNCONTROLLED

3.7. Sample Duplicate - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures The purpose is to verify the precision associated with the laboratory procedures

3 8 Matrix Spike - aliquots of sample to which known amounts of an analyte of interest has been added These are treated exactly the same throughout laboratory analytical procedures The purpose of a matrix spike is to determine whether the sample matrix contributes bias to the analytical results

COPY

3 9 Analytical Run Sequence - Samples are analyzed in a set referred to as an analysis sequence The sequence begins with the instrument calibration or calibration verification followed by samples interspersed with calibration standards The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded

4 INTERFERENCES

4 1 Calcium and magnesium ions may precipitate if present in sufficient concentration Tartrate or EDTA is added to the sample in-line in order to prevent this problem

4 2 Color, turbidity and certain organic species may interfere Turbidity is removed through manual filtration

4 3 Over-acidic samples create a negative interference resulting in an inverted peak with samples that are at or near the method reporting limit

4 4 Ensure that the pH of the dilution water and standard NH_3 solution approximates that of the sample

5 SAFETY

5 1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment such as, safety glasses, lab coat and the correct gloves

5 2 Chemicals reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method

5 3 Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard Use nitrile or latex gloves while handling pellets or preparing solutions

UNCONTROLLED

5 4 Phenol causes severe burns and is an extreme health hazard through skin absorption Wear proper protective laboratory clothing including gloves and rinse any exposed skin IMMEDIATELY with copious amounts of water

6 SAMPLE HANDLING AND PRESERVATION

6 1 Water samples

6 1 1 Samples should be collected in plastic or glass bottles Bottles must be purchased as pre cleaned containers or thoroughly cleaned and rinsed with reagent water The volume collected should be sufficient to insure a representative sample, allow for replicate analysis

COPY

6 1 2 Water samples are preserved immediately upon sampling or as soon as possible with H_2SO_4 to pH <2 and stored at 4±2° C until time of analysis Analysis is to be performed within 28 days of sampling

6 2 Soils/sediment samples

6 2 1 Samples should be collected in glass jars and stored in a field-moist condition Ammonia may be lost by volatilization due to drying or thawing

6 2 2 Extraction is to be performed within 7 days of sampling Extracts may be preserved with 9N sulfuric acid and stored for up to 28 days until analysis

7 APPARATUS

7 1 Easy-Still Ammonia Distillation Apparatus Components are boiling tubes, sloped T-joints, glass stoppers, Allihn condensers and condenser stems

7 2 Flow Injection Analyzer with associated software and computer system The two systems currently in use are listed below

7 2 1 Lachat QuikChem AE

7 2 2 Bran & Luebbe AutoAnalyzer

7 3 Heating unit associated with the FIA

7 4 Wrist Action Shaker

7 5 Filter Funnel and Whatman 934 AH or equivalent

7 6 Glassware

UNCONTROLLED

7 6 1 Standard laboratory glassware

7 6 2 Class A volumetric flasks and pipettes

8 REAGENTS

8 1 Dechlorinating reagents

8 1 1 Sodium thiosulfate Dissolve 3 5g $Na_2S_2O_3 \cdot 5H_2O$ in reagent water and dilute to 1L One mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample

COPY

8 1 2 Sodium sulfite Dissolve 0 9 g Na_2SO_3 in reagent water and dilute to 1L One mL removes 1 mg/L Cl per 500 mL of sample

8 2 Sodium Hydroxide Solution, 6N, dissolve 48 g of NaOH pellets in 150 ml deionized water Dilute to 200 ml, cool and store in plastic container

8 3 KCl, 2M, dissolve 150g of KCl in 1L deionized water

8 4 Boric Acid Solution, 2% (w/v), dissolve 20 0 g of H3BO3 in deionized water Dilute to final volume of 1,000 ml

8 5 Sulfuric acid, 0 04N 1 1 mL of concentrated sulfuric acid to 1L DI water

8 6 Sulfuric acid 9N

8 7 Lachat analyses

8 7 1 Sodium Phenolate Add 83 0g phenol crystals to a 1L volumetric flask containing approximately 500mL of deionized water (DIW) Slowly add 32 0 g NaOH to the

stirring phenolate mixture Cool, dilute to the mark with DIW, and invert several times to mix Do not allow solution to stand in hood for excessive amount of time Refrigerate after use Do not degas this reagent

CAUTION Phenol causes severe burns and is an extreme health hazard through skin absorption Wear proper protective laboratory clothing including gloves and rinse any exposed skin IMMEDIATELY with copious amounts of water

8 7 2 Sodium Hypochlorite Mix 200 mL of Ultra Clorox Bleach (only this brand is recommended) to 250 mL of DIW Make fresh daily

UNCONTROLLED

8.7 3 Buffer In a 1 L volumetric flask dissolve 50 0 g disodium ethylenediamine tetraacetate (Na_2 EDTA) and 5 5 g NaOH in approximately 900mL of DIW Dilute to the mark and invert several times to mix Make monthly

8 7 4 Sodium Nitroprusside (nitroferricyanide) Dissolve 3 50 g sodium nitroprusside in a 1L volumetric containing DIW Dilute to mark and invert to mix Do not degas this reagent

8 7 5 2M Potassium Chloride (KCl) Dissolve 597 g of potassium chloride in DIW and take to a 4 L final volume

COPY

8 8 Bran & Luebbe analyses - For analysis performed on the Bran & Luebbe analyzer, refer to the Barn & Luebbe method attachment for reagents used and preparation instructions

8 9 Stock Standard 10,000 mg/L In a 1L volumetric flask containing approximately 800 mL of DIW dissolve 38 19 g of ammonium chloride (NH_4Cl) that has been dried for two hours at 110° C Dilute to the mark and invert to mix

8 10 Working Standard 100 mg/L To a 100 mL volumetric flask containing DIW add 1 mL of 10,000 ppm stock standard Dilute to the mark

8 11 Calibration standards See Table 1

Note Standards for soil extracts are prepared as in table 1, except that the standards are prepared in 2M KCL INSTEAD of DIW

8 12 Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should approximate that of the samples

9 RESPONSIBILITIES

9 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

9 2 It is the responsibility of the department supervisor/manager to document analyst training Training and proficiency is documented in accordance with the SOP for Documentation of Training (ADM-TRANDOC)

UNCONTROLLED

10 PREVENTIVE MAINTENANCE

10 1 No specific maintenance steps are needed other than normal cleaning and inspection of apparatus

10 2 Change reagent and sampling lines when they are flat

10 3 For problems encountered with the analyzer operation, refer to the applicable manufacturer's operating and/or troubleshooting information (Lachat troubleshooting guide, Bran&Luebbe manual)

11 PROCEDURE

COPY

11 1 Sample preparation – water samples

Note NPDES final effluent samples must be distilled unless otherwise allowed or approved by the client The distilled results are compared to non-distilled results If the results are considered equivalent, distillation of subsequent samples of the same effluent is not required All comparative studies are performed on a client basis and all associated data is kept on file in the General Chemistry lab

11 1 1 Sample Dechlorination - If the water sample contains residual chlorine, add a dechlorination agent, such as sodium thiosulfate or ascorbic acid, to the sample Check for residual chlorine by placing a drop of sample on potassium-iodide test paper Samples should be dechlorinated at the time of collection

11 1 2 Adjust the pH of a 50-ml sample aliquot to pH 9 5 Add 6 N NaOH dropwise, with mixing, to the sample to adjust the sample pH to 9 5 Check the sample pH with a narrow range pH paper Add 2 5 ml borate buffer solution, mix sample Check pH and re adjust sample to final pH of 9 5 if necessary

11 1 3 Place the pH adjusted sample in a boiling tube Add 2-3 micro-porous boiling stones Assemble the distillation apparatus in the heater block

11 1 4 Place 5 0 ml of receiving solution in 50-ml centrifuge tube Place the centrifuge tube in the base slot of the heating block Select the receiver solution according to analysis method to be used on distillate

11 1 5 Place the condenser stem in the centrifuge tube, slide cylinder and stem under condenser, and connect stem to condenser with WestClip When assembled, the condenser tip of the distillation apparatus will be submerged in the receiving solution contained in the centrifuge tube

11 1 6 Heat the distillation apparatus - Set heater block temperature controls to the following settings

UNCONTROLLED

RATE1:	15 °C/min	RATE2	0
TEMP1	210 °C	TEMP2:	210°C
TIME1	2 0 Hour (max)	TIME2	0

Timing Configuration CONF1

11 1 7 Collect a minimum of 20 ml if distillate

11 1 8 Discontinue heating Remove the stopper from the top of the "T" joint The stopper removal is needed to prevent the collected distillate from being sucked back into the apparatus during cooling

COPY

11 1 9 Disconnect the stem from the condenser Remove the graduated cylinder from the apparatus and dilute the collected distillate to final volume of 50 ml with deionized water

11 2 Soil sample extraction

11 2 1 1 Weigh out 10 g of sample into a 50 mL centrifuge tube

11 2 1 2 Spike appropriate QC sample with 0 5 mL of 10,000 ppm NH_3 stock solution

11 2 1 3 Bring to 50mL volume with 2M KCl The Method blank contains only KCl

11 2 1 4 Shake samples for 30 minutes on the wrist-action shaker

11 2 1 5 Centrifuge samples for 10-20 minutes

11 2 1 6 Filter supernatant with 0 45μm filter Samples are now ready for analysis

11 3 Soil and sediment extraction - Plumb extraction procedure

11 3 1 1 Weigh 20g of sample into a 50mL centrifuge tube

11 3 1 2 Spike appropriate QC sample with 1 0 mL of 10,000 ppm NH_3 stock solution

11 3 1 3 Bring to 50mL volume with 2M KCl The Method blank contains only KCl

UNCONTROLLED

11 3 1 4 Shake samples for 30 minutes on the wrist-action shaker

11 3 1 5 Centrifuge samples for 10-20 minutes

11 3 1 6 Filter supernatant with 0 45μm filter into a 100mL volumetric flask

11 3 1 7 Wash the remaining solids with an additional 50mL of 2M KCl and filter into the volumetric flask Bring to volume with 2M KCl Samples are now ready for analysis

11 4 Sample analysis - Lachat system

COPY

11 4 1 Set up instrument according to the Lachat QuikChem method 10-107-06-1-B (See Attachments)

Note 2M KCl may be used for a sample carrier when running extracts instead of DIW

11 4 2 The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument The verification of linearity must use a minimum of a blank and three standards If any verification data exceeds the initial values by ±10%, linearity must be reestablished If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion

11 4 3 Analyze the calibration standards listed in Table 1 The calibration curve is fitted to a linear, least squares model See Appendix A The correlation coefficient must be > 0 995 If the calibration criteria are met, continue with the analysis sequence in Table 2 If the LCS recovery is acceptable, proceed with analysis of samples If not, determine the cause of the problem, correct it, and then recalibrate

11 4 4 Place samples and QC aliquots in sampler vials and arrange on autosampler according to Table 2

11 4 5 Repeat sequence bracketing every 10 samples with CCV and CCB End the sample tray (sequence) with CCV and CCB

11 5 Sample analysis – Bran&Luebbe system

11 5 1 Set up instrument according to the Bran&Luebbe method US 696D-82X (See Attachments)

UNCONTROLLED

Note: 2M KCl may be used for a sample carrier when running extracts instead of DIW

11 5 2 The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument The verification of linearity must use a minimum of a blank and three standards If any verification data exceeds the initial values by ±10% linearity must be reestablished If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion

COPY

11 5 3 Analyze the calibration standards listed in Table 1 (regular level) or Table 2 (low level) The calibration curve is fitted to a linear least squares model See Appendix A The correlation coefficient must be > 0 995 If the calibration criteria are met, continue with the analysis sequence in Table 2 If the LCS recovery is acceptable, proceed with analysis of samples If not, determine the cause of the problem, correct it, and then recalibrate

11 5 4 Ensure that the pH of the dilution water and standard NH_3 solution approximates that of the samples Place samples and QC aliquots in sampler vials and arrange on autosampler according to Table 3

11 5 5 Repeat sequence bracketing every 10 samples with CCV and CCB End the sample tray (sequence) with CCV and CCB

12 QA/QC REQUIREMENTS

12 1 Initial Precision and Recovery Validation - The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made To do this, four LCS aliquots are prepared and analyzed The average percent recovery must be 85-115% and the RSD< 30%

12 2 Method Detection Limits - A method detection limit (MDL) study must be undertaken before analysis of samples can begin To establish detection limits that are precise and accurate, the analyst must perform the following procedure Spike a minimum of seven blank replicates at a level near or below the MRL Follow the procedures starting in Section 11 to analyze the samples Refer to the CAS *SOP for The Determination of Method Detection Limits*

12 3 CCV (Continuing Calibration Verification) A CCV is analyzed every 10 samples using 2 0 mg/L NH3 standard (from curve) Recovery must fall within 90-110% or 1 8-2 2 mg/L

UNCONTROLLED

12 4 CCB (Continuing Calibration Blank) A blank consisting of the carrier solution (DIW or KCl). The result must be less than the absolute value of the Method Reporting Limit |MRL|.

12 5 LCS (Laboratory Control Spike) Analyzed with each batch of 20 or fewer samples An LCS must be run each day samples are analyzed and have a recovery of 90-110% of true value

12 6 MB (Method Blank) Deionized water or KCl depending upon samples being analyzed, run every 20 or fewer samples The result must be less than the absolute value of the Method Reporting Limit - |MRL|

COPY

12 7 Sample Duplicates One sample per batch of 20 or less samples must be analyzed in duplicate

12 8 Matrix Spike One spiked sample must be analyzed with each batch of 20 or less samples The spiked sample is usually the same sample used for the duplicate The recovery criteria is 90-110% for waters and 75-125% for soils

13 DATA REDUCTION, REVIEW, AND REPORTING

13 1 At the end of the analysis sequence, the calibration data is printed including the calculated standards concentrations, calibration statistics, and slope and intercept of the calibration curve

13 2 The runtime report printed during the sampling run is turned in with a final report and calibration report

13 3 For water samples the postrun report is saved to disk and prepared on EXCEL

13 4 The postrun report for soils is printed at the Lachat, and the numbers transposed to the appropriate bench sheet Results are calculated on the bench sheet with dry weights

13 5 Report results to three significant figures If sample was diluted report two significant figures

13 6 Soil/sediment samples and undistilled water samples should be reported as method 350 1 Modified

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements.

UNCONTROLLED

15 METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

16 POLLUTION PREVENTION

COPY

It is the laboratory s practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly

17 WASTE MANAGEMENT

17 1 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual

17 2 This method uses acid Waste acid is hazardous to the sewer system and to the environment All acid waste must be neutralized to a pH of 2 5 12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record See the CAS EH&S Manual for details

17 3 This method uses a base Waste base is hazardous to the sewer system and to the environment All waste must be neutralized to a pH of 2 5 12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record See the CAS EH&S Manual for details

18 REFERENCES

18 1 U S Environmental Protection Agency, *Methods for Chemical Analyses of Water and Wastewater*, EPA-600/4-79-020, March 1983 - Method 350 1

18 2 Methods 4500-NH_3 B,G, *Standard Methods for the Examination of Water and Wastewater*, 20th Ed , 1998

18 3 Lachat QuikChem Method 10-107-06-1-B

18 4 Bran & Luebbe Method US-696D 82X

18 5 *Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound*, January, 1996

18 6 *Procedures for Handling and Chemical Analysis of Sediment and Water Samples* Russell S Plumb, U S EPA/Corps of Engineers Technical Committee on Criteria for Dredged Fill Material, May 1981

UNCONTROLLED

COPY

TABLE 1
Calibration Standards Preparation
Regular Level Ammonia

Routine Calibration Standards

Volume of 100 µg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0	100	0 00
0 05	100	0 10
0 50	100	0 20
2 00	100	1 00
4 00	100	3 00

UNCONTROLLED

TABLE 2
Calibration Standards Preparation
Low Level Ammonia

Low Level Calibration Standards

Volume of 10 µg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0	100	0 00
0 10	100	0 01
0 50	100	0 05
2 50	100	0 25
5 00	100	0 50

COPY

Note For low level analysis change sample tubing from 0 16"ID (orn/yel) to 0 42"ID (orn/orn)

TABLE3
Analytical Run Scheme

Step	Sample
1	CCV 1
2	CCB 1
3	Method Blank
4	LCS
5	Sample
6	Sample Dup
7	Sample Spike
8	Sample
9	Sample
10	Sample
11	Sample
12	Rinse Blank
13	CCV 2
14	CCB 2
15	9 more Samples
16	CCV 3
17 26	CCB 3

Repeat steps 5 28 for remainder of samples

UNCONTROLLED
COPY

APPENDIX A

The calibration is determined using a linear regression that best fits the line of the X Y pairs The quality of the fit is determined by calculating the coefficient of determination (R2), also called the correlation coefficient

The line of regression is calculated as follows

Start with the equation for a line, y = mx + b. From here the line of regression can be determined

UNCONTROLLED

$$m = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - \left(\sum x\right)^2}$$

$$b = \frac{\sum y - m\sum x}{n}$$

COPY

Where

x = the values of the x variables
y = the values of the y variables
n = the number of data points

Once the line of regression has been determined then the coefficient of determination can be calculated

$$r^2 = \frac{\left(\sum xy - n\overline{x}\,\overline{y}\right)^2}{\left(\sum x^2 - \overline{x}\sum x\right) * \left(\sum y^2 - \overline{y}\sum y\right)}$$

ATTACHMENTS

Lachat and Bran & Luebbe Methods

UNCONTROLLED

COPY

QuikChem METHOD 10-107-06-1-B

DETERMINATION OF AMMONIA (PHENOLATE) BY FLOW INJECTION ANALYSIS COLORIMETRY

UNCONTROLLED

Written by William R Prokopy

Applications Group

COPY

Revision date

24 December 1993

LACHAT INSTRUMENTS

6645 WEST MILL ROAD

MILWAUKEE WI 53218 USA

LACHAT

INSTRUMENTS

QuikChem Method 10-107-06-1-B

Ammonia (Phenolate) in Potable and Surface Waters

UNCONTROLLED

0.01 to 2 0 mg N/L

-- Principle --

This method is based on the Berthelot reaction Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample

COPY

-- Interferences --

1 Calcium and magnesium ions may precipitate if present in sufficient concentration Tartrate or EDTA is added to the sample in-line in order to prevent this problem

2 Color, turbidity and certain organic species may interfere Turbidity is removed by manual filtration

-- Special Apparatus --

1 Heating Unit

Revised by Karin Wendt/KS and copyrighted © on 24 December 1993 by Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, USA Phone 1 414 358 4200 FAX 1 414 358 4206 This document is the property of Lachat Instruments Unauthorized copying of this document is prohibited

METHOD CONTENTS

1	SCOPE AND APPLICATION	3
2	SUMMARY OF METHOD	3
3	DEFINITIONS	3
4	INTERFERENCES	4
5	SAFETY	4
6	EQUIPMENT AND SUPPLIES	5
7	REAGENTS AND STANDARDS	5
8	SAMPLE COLLECTION, PRESERVATION AND STORAGE	7
9	QUALITY CONTROL (USEPA guideline)	8
10	CALIBRATION AND STANDARDIZATION	11
11	PROCEDURE	11
12	DATA ANALYSIS AND CALCULATIONS	12
13	METHOD PERFORMANCE	13
14	POLLUTION PREVENTION	13
15	WASTE MANAGEMENT	13
16	REFERENCES	14
17	TABLE, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA	15

UNCONTROLLED COPY

QUIKCHEM METHOD 10-107-06-1-B

DETERMINATION OF AMMONIA BY FLOW INJECTION ANALYSIS COLORIMETRY

1. SCOPE AND APPLICATION

1 1 This method covers the determination of ammonia in potable and surface waters

1 2 The method is based on reactions that are specific for ammonia

1 3 The applicable range is 0 01 to 2 0 mg N/L The method detection limit is 0 006 mg N/L Approximately 70 samples per hour can be analyzed

UNCONTROLLED

2 SUMMARY OF METHOD

2 1 Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample

3. DEFINITIONS

3 1 CALIBRATION BLANK (CB) -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes

COPY

3 2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3 3 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria

3 4 LABORATORY FORTIFIED BLANK (LFB) -- an aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements

3 5 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory The LFM is analyzed exactly like sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results The background

concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations

3 6 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment solvents, reagents, internal standards and surrogates that are used with other samples The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus

3 7 LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear

3 8 MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties fire, and reactivity data including storage, spill, and handling precautions

UNCONTROLLED

3 9 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified measured and reported with 99% confidence that the analyte concentration is greater than zero

3 10 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix The QCS is obtained from a source external to the laboratory and different from the source of calibration standards It is used to check laboratory performance with externally prepared test materials

COPY

3 11 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source

4 INTERFERENCES

4 1 Calcium and magnesium ions may precipitate if present in sufficient concentration Tartrate or EDTA is added to the sample in-line in order to prevent this problem

4 2 Color, turbidity and certain organic species may interfere Turbidity is removed by manual filtration

5 SAFETY

5 1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable Cautions are included for known extremely hazardous materials

5 2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method A reference file of Material Safety Data sheets (MSDS) should be made available to all

personnel involved in the chemical analysis The preparation of a formal safety plan is also advisable

5 3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS

5 3 1 Phenolate

5 3 2 Nitroferricyanide

6. EQUIPMENT AND SUPPLIES

6 1 Balance -- analytical, capable of accurately weighing to the nearest 0 0001 g

UNCONTROLLED

6 2 Glassware -- Class A volumetric flasks and pipettes or plastic containers as required Samples may be stored in plastic or glass

6 3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios

6 3 1 Autosampler

6 3 2 Multichannel proportioning pump

6 3 3 Reaction unit or manifold

COPY

6 3 4 Colorimetric detector

6 3 5 Data system

6 4 Special apparatus

6 4 1 Heating Unit

7. REAGENTS AND STANDARDS

7 1 PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions

Degassing with helium

To prevent bubble formation, degas all solutions except the standards with helium Use He at 140 kPa (20 lb/in^2) through a helium degassing tube (Lachat Part 50100) Bubble He vigorously through the solution for one minute

Reagent 1 Sodium Phenolate

CAUTION Wear gloves Phenol causes severe burns and is rapidly absorbed into the body through the skin

By Volume In a 1 L volumetric flask dissolve 88 mL of 88% liquified phenol or 83 g crystalline phenol (C_6H_5OH) in approximately 600 mL water While stirring, slowly add 32 g sodium hydroxide (NaOH) Cool, dilute to the mark, and invert three times Do not degas this reagent

By Weight To a tared 1 L container, add 888 g water Add 94 2 g of 88% liquified phenol or 83 g crystalline phenol (C_6H_5OH) While stirring slowly add 32 g sodium hydroxide (NaOH) Cool and invert three times to mix thoroughly Do not degas this reagent

UNCONTROLLED

Reagent 2 Sodium Hypochlorite

By Volume In a 500 mL volumetric flask dilute 250 mL Regular Clorox bleach [5 25% sodium hypochlorite (NaOCl), The Clorox Company Oakland CA] to the mark with water Invert to mix

By Weight To a tared 500 mL container add 250 g Regular Clorox bleach [5 25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland CA] and 250 g water Stir or shake to mix

COPY

Reagent 3 Buffer

By Volume In a 1 L volumetric flask, dissolve 50 0 g disodium ethylenediamine tetraacetate (Na_2EDTA) and 5 5 g sodium hydroxide (NaOH) in approximately 900 mL water Dilute to the mark and mix with a magnetic stirrer until dissolved

By Weight To a 1 L tared container add 50 0 g disodium ethylenediamine tetraacetate (Na_2EDTA) and 5 5 g sodium hydroxide (NaOH) Add 968 g water Mix with a magnetic stirrer until dissolved

Reagent 4 Sodium Nitroprusside

By Volume To a 1 L volumetric flask dissolve 3 50 g sodium nitroprusside (Sodium Nitroferricyanide [$Na_2Fe(CN)_5NO\ 2H_2O$]) dilute to the mark with water and invert to mix

By Weight To a tared 1 L container add 3 50 g sodium nitroprusside (Sodium Nitroferricyanide [$Na_2Fe(CN)_5NO\ 2H_2O$]) and 1000 g water Invert to mix

7 2 PREPARATION OF STANDARDS

Standard 1 Stock Standard 1000 mg N/L

In a 1 L volumetric flask dissolve 3 819 g ammonium chloride (NH_4Cl) that has been dried for two hours at 110°C in about 800 mL water Dilute to the mark with DI water and invert to mix

Standard 2 Working Stock Standard Solution 20 0 mg N/L

By Volume In a 1 L volumetric flask, add 20 0 mL Stock Standard (Standard 1) to the mark with water Invert to mix

UNCONTROLLED

By Weight To a tared 1 L container add about 20 g Stock Standard (Standard 1) Divide the actual weight of the solution added by 0 02 and make up to this resulting total weight with water Invert to mix

Set of Eight Working Standards

2 00	0 80	0 20	0 100	0 040	0 020	0 010	0 00	mg N/L

By Volume To eight 250 mL volumetric flasks add, respectively,

COPY

25 0	10 0	2 50	1 25	0.50	0 250	0 125	0 0	mL

Standard 2 Dilute each to the mark with water invert to mix

By Weight To eight tared 250 mL containers add respectively, about

25 0	10 0	2 50	1 25	0 50	0 250	0 125	0 0	g

Standard 2 Take the exact weight obtained for each and divide by

0 10	0 04	0 01	0 005	0 002	0 001	0 0005

to get the total weight of the diluted solution Make up each solution to this total weight with water Shake before using

If samples always fall within a narrower range, more standards within this narrower range can be added and standards outside this narrower range can be dropped

8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8 1 Samples should be collected in plastic or glass bottles All bottles must be thoroughly cleaned and rinsed with reagent water volume collected should be sufficient to insure a

representative sample, allow for replicate analysis (if required) and minimize waste disposal

8 2 Ammonia is volatile and will leave the sample slowly, even through polyethylene bottles The samples should be run within 24 hours If this cannot be done, they should be frozen If this cannot be done, the samples should be adjusted to a pH of 3-5 with dilute phosphoric or sulfuric acid The Federal Register entry which defines standard EPA NPDES and NPDWR methods states that "Manual Distillation is NOT required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary however, manual distillation will be required to resolve any controversies" (see SOURCES) This suggests that the user perform recovery studies on representative sample types, studies which show that the undistilled samples give the same recoveries as the manually distilled samples Follow EPA Method 350 2 for the complete distillation procedure.

UNCONTROLLED

9. QUALITY CONTROL (USEPA GUIDELINE)

9 1 Each laboratory using this method is required to operate a formal quality control (QC) program The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance The laboratory is required to maintain performance records that define the quality of the data that are generated

COPY

9 2 INITIAL DEMONSTRATION OF PERFORMANCE

9 2 1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method

9 2 2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear The verification of linearity must use a minimum of a blank and three standards If any verification data exceeds the initial values by +/- 10%, linearity must be nonlinear sufficient standards must be used to clearly define the nonlinear portion

9 2 3 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS If the determined concentrations are not within +/-10% of the stated values performance of the determinative step of the method is unacceptable The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses

9 2 4 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method Perform all calculations defined in the method and report the concentration values in the appropriate units Calculate the MDL as follows

$$MDL = (t) \times (S)$$

Where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3 14 for seven replicates, t= 2 528 for twenty one replicates] S = standard deviation of the replicate analyses

UNCONTROLLED

MDLs should be determined every 6 months, when a new operator begins work or whenever there is a significant change in the background or instrument response

9 3 ASSESSING LABORATORY PERFORMANCE

9 3 1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples Data produced are used to assess contamination from the laboratory environment Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis

COPY

9 3 2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples Calculate accuracy as percent recovery (Sect 9 4 2) If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses

9 3 3 The laboratory must used LFB analyses data to assess laboratory performance against the required control limits of 90-110% When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (X) and the standard deviation (S) of the mean recovery These data can be used to establish the upper and lower control limits as follows

$$\text{UPPER CONTROL LIMIT} = \overline{X} + 3S$$

$$\text{LOWER CONTROL LIMIT} = \overline{X} - 3S$$

The optional control limits must be equal to or better than the required control limits of 90-110% After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB These data must be kept on file and be available for review

9 3 4 Instruments Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within +/-10% of calibration Subsequent analyses of the IPC solution must verify the calibration is still within +/-10% If the calibration cannot be verified within the specified limits, reanalyze the IPC solution If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated All samples following the last acceptable IPC solution must be reanalyzed The analysis data of the calibration blank and IPC solution must be kept on file with sample analyses data

UNCONTROLLED

9 4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9 4 1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of routine samples In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL The added analyte concentration should be the same as that used in the laboratory fortified blank

9 4 2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110% Percent recovery may be calculate using the following equation

COPY

$$R = \frac{C_s - C}{s} X100$$

Where, R = percent recovery

C_s = fortified sample concentration

C = sample background concentration

s = concentration equivalent of analyte added to sample

9 4 3 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (sect 9 3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related

9 4 4 Where reference materials are available, they should be analyzed to provide additional performance data The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably

10. CALIBRATION AND STANDARDIZATION

10 1 Prepare a series of standards, covering the desired range, and a blank by diluting suitable volumes of standard solution (suggested range in section 7 2)

10 4 Calibration the instrument as description in section 11

10 2 Prepare standard curve by plotting instrument response against concentration values A calibration curve may be fitted to the calibration solution concentration/response data using the computer Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration

10 3 After the calibration has established, it must be verified by the analysis of a suitable quality control sample (QCS). If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument recalibrated The new calibration must be verified before continuing analysis Periodic reanalysis of the QCS is recommended as a continuing calibration check

UNCONTROLLED COPY

11. PROCEDURE

11 1 Calibration Procedure

11 2 1 Prepare reagent and standards as described in section 7

11 2 2 Set up manifold as shown in section 17 1

11 2 3 Input peak timing and integration window parameters as below

Sample throughput		**72 samples/h, 50 s/sample**
Pump speed		**35**
Cycle period		**72 s**
Inject to start of peak period		**22 s**
Inject to end of peak period		**68 s**
Presentation Data Window		
Top Scale Response		**0 50 abs**
Bottom Scale Response		**0 00 abs**
Segment/Boundaries	A	**2 00 mg N/L**
	D	**0 10 mg N/L**

G 0 01 mg N/L

H 0 00 mg N/L

Series 4000/System IV Settings Gain = 500 x 1

11 2 4 Pump DI water through all reagent lines and check for leaks and smooth flow Switch to reagents and allow the system to equilibrate until a stable baseline is achieved

11 2 5 Place standards in the autosampler, and fill the sample tray Input the information required by data system, such as concentration replicates and QC scheme

UNCONTROLLED

11 2 6 Calibrate the instrument by injecting the standards The data system will then associate the concentrations with responses for each standard

11 3 Analysis Procedure

11 3 1 After a stable baseline has been obtained, start the sampler and perform analysis (please refer to system notes)

11 4 System Notes

11 4 1 Allow 15 min for heating unit to warm up to 60°C

COPY

11 4 2 If baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure

A Place all reagent lines in deionized water and pump to clear reagents (2 to 5 min)

B Place all reagent lines in 1 M hydrochloric acid (1 volume concentrated HCl added to 11 volumes of deionized water) and pump for several minutes

C Place all reagent lines in deionized water and pump until the HCl is thoroughly washed out

D Resume pumping reagents

12 DATA ANALYSIS AND CALCULATIONS

12 1 Prepare a calibration curve by plotting instrument response against standard concentration Compute sample concentration by comparing sample response with the standard curve

12 2 Report only those values that fall between the lowest and the highest calibration standards Samples exceeding the highest standard should be diluted and reanalyzed Any sample whose computed value is less than 5% of its immediate predecessor must be rerun

12 3 Report results in mg N/L

13. METHOD PERFORMANCE

13 1 The method performance data are presented as method support data in section 17 2 This data was generated according to Lachat Standard Operating Procedure J001, Lachat FIA Support Data Generation

14. POLLUTION PREVENTION

UNCONTROLLED COPY

14 1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation Numerous opportunities for pollution prevention exist in laboratory operation The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option

14 2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material Actual reagent preparation volumes should reflect anticipated usage and reagent stability

14 3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better Laboratory Chemical Society's Department of Government Regulations and Science Policy, 115 16th Street N W , Washington D C 20036, (202) 872-4477

15 WASTE MANAGEMENT

15 1 The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner The agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waster discharge permit and regulations, and by complying with all solid and hazardous waste regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Sect 14 3

16 REFERENCES

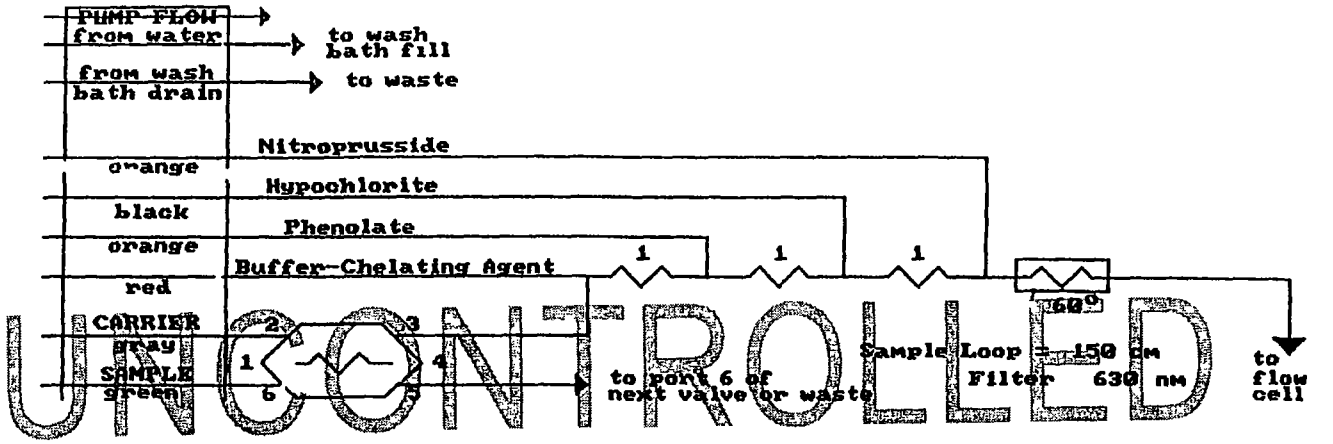
16 1 U S Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes* EPA 600/4-79-020 Revised March 1983, Method 350 1

UNCONTROLLED

COPY

17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17 1 MANIFOLD DIAGRAM



UNCONTROLLED COPY

CARRIER is **Water**

1" is **70 0** cm of tubing on a 1 in coil support

2" is **135** cm of tubing on a 2 in coil support

APPARATUS Standard valve, flow cell and detector head modules are used The box shows **650 cm of heated tubing.**

All manifold tubing is **0 8 mm (0 032 in) i d** This is **5 2 uL/cm**

MANIFOLD DIAGRAM REVISION DATE 12 August 1993 by N Liao

17 2 SUPPORT DATA

17 2 1 Support Data

QuikChem AE Calibration Report for Calibration 93121001
M thod: a e ia 10-107-06 1-8
This calibration s first done or last modified on 12/10/93 at 12:13 pm
This report pr pared on 12/10/93 at 01:18 p

Analyte	Units	Average Concentrations Known	Determined	% Residual	Baseline Corrected Average Absorbance
andard A, a monia	mg N/L	2.000	1 991	0.46	0.1157
andard B, ammonia	mg N/L	0.800	0.822	-2.77	0.0480
andard C, am onia	mg N/L	0.200	0.207	-3.63	0.0123
andard D, ammonia	mg N/L	0.100	0.096	3.71	0.0059
andard E, ammonia	mg N/L	0.040	0.040	-0.65	0.0026
andard F am onia	mg N/L	0.020	0.014	30.81	0.0011
ammonia	g N/L	0.010	0.010	0.00	0.0006
andard H, ammonia	g N/L	0.000	0.000	*** **	-0.0000

Calibration Statistics Report

Cal Ref: 93121001
Method: AMMONB

12/10/93 01:21 pm

Channel: ammonia

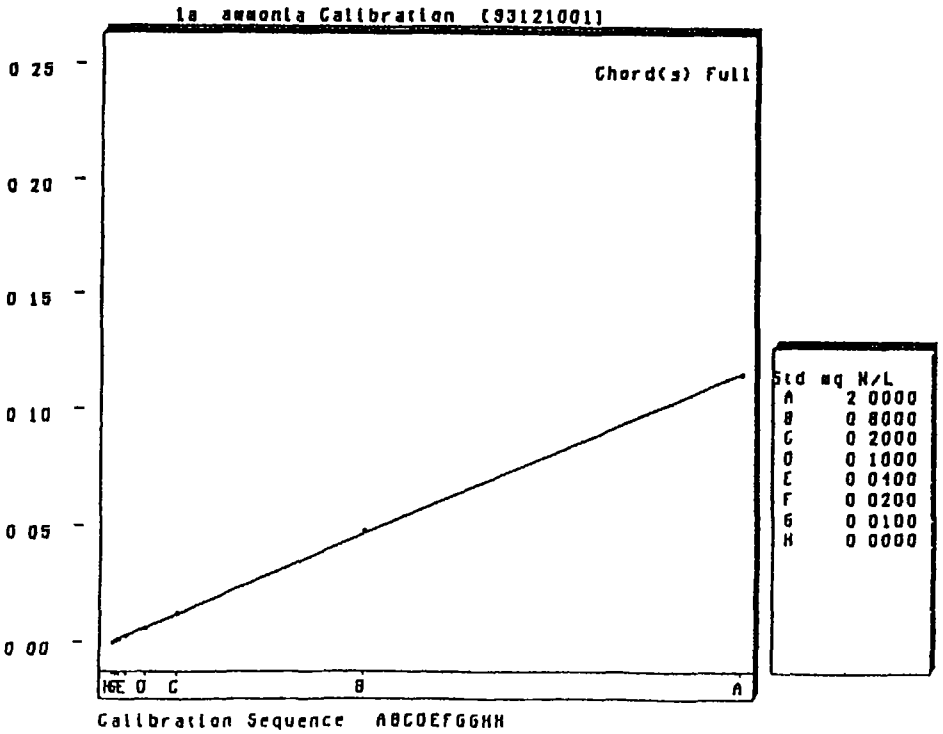
Correlation Coefficients

Seg	Stds	Full	Chord 1	Chord 2	Chord 3	Chord 4	Chord 5
1	A-G	0 9998	0 9772 ?	0 9998	0 9997	0 9998	0 9994
2	G-H	0 9910	0 7363 ?	0 9787 ?	0 9953	0 9911	0 2604 ?

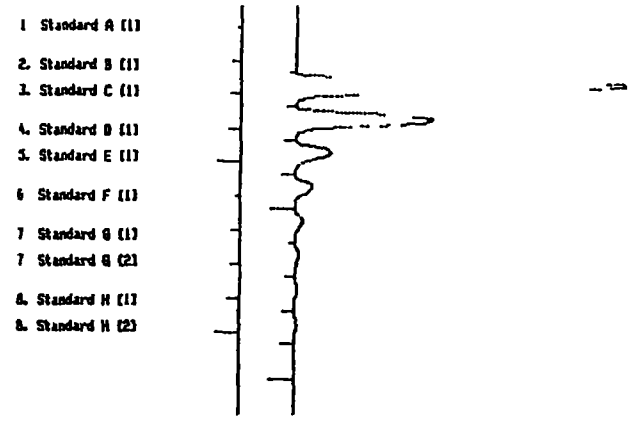
Percent Standard Deviation in Slope

1	A-G	0 6	6 2	0 5	0 8	0 5	1 0
2	G-H	6 7	42 3	10 4	4 8	6 7	119 2 ?

UNCONTROLLED COPY

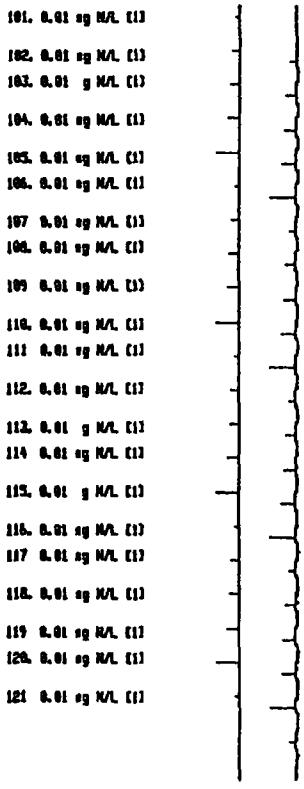


Calibration 12/10/1993 12:01 pm



UNCONTROLLED

Rack 1 (Ref: 93121001) 12/10/1993 12:17 pm



COPY

Cupt	Sample ID		ammonia mg N/L
101	0.01	mg N/L	0.010
102	0.01	mg N/L	0.009
103	0.01	mg N/L	0.009
104	0.01	mg N/L	0.009
105	0.01	mg N/L	0.012
106	0.01	mg N/L	0.011
107	0.01	mg N/L	0.012
108	0.01	mg N/L	0.011
109	0.01	mg N/L	0.010
110	0.01	mg N/L	0.010
111	0.01	mg N/L	0.011
112	0.01	mg N/L	0.011
113	0.01	mg N/L	0.010
114	0.01	mg N/L	0.011
115	0.01	mg N/L	0.010
116	0.01	mg N/L	0.008
117	0.01	mg N/L	0.011
118	0.01	mg N/L	0.012
119	0.01	mg N/L	0.013
120	0.01	mg N/L	0.012
121	0.01	mg N/L	0.009

MDL

= 0.011 mg N/L

s = 0.0013

MDL = 0.003 mg N/L

Rack 1 (Ref: 93121002) 12/10/1993 12:48 pm

101 0.1 mg N/L [1]
102. 0.1 mg N/L [1]
103. 0.1 g N/L [1]
104 0.1 g N/L [1]
105. 0.1 mg N/L [1]
106 0.1 mg N/L [1]
107 0.1 g N/L [1]
108. 0.1 mg N/L [1]
109 0.1 g N/L [1]
110 0.1 mg N/L [1]

Cupt Sample ID	mg N/L
101 0.1 mg N/L	0.104
102 0.1 g N/L	0.106
103 0.1 mg N/L	0.109
104 0.1 mg N/L	0.106
105 0.1 mg N/L	0.103
106 0.1 mg N/L	0.102
107 0.1 mg N/L	0.105
108 0.1 mg N/L	0.106
109 0.1 mg N/L	0.107
110 0.1 mg N/L	0.105

Precision

x = 0.105 mg N/L

s = 0.002

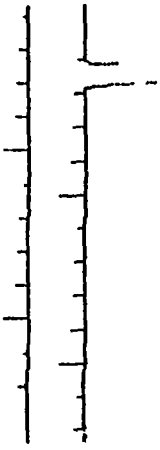
RSD = 1.90%

UNCONTROLLED

COPY

Rack 1 (Ref: 93121003) 12/10/1993 01:01 pm

101 2 mg N/L [1]
102. blank [1]
103. blank [1]
104 blank [1]
105. blank [1]
106 blank [1]
107 blank [1]
108. blank [1]
109 blank [1]
110. blank [1]
111 blank [1]
112. blank [1]



Cupt Sample ID	mg N/L
101 2 mg N/L	2.072
102 blank	-0.002
103 blank	0.000
104 blank	-0.001
105 blank	-0.001
106 blank	0.001
107 blank	0.000
108 blank	0.001
109 blank	-0.000
110 blank	0.000
111 blank	-0.003
112 blank	-0.001

Carryover

x = 0.0004 mg N/L

s = 0.0012

t = 2.262

-0.0004 +/ 0.0009

EMDL

s = 0.0012

EMDL = 0.006 mg N/L

BRAN+LUEBBE
1025 Busch Parkway Buffalo Grove IL 60089
(847) 520 0700
FAX (847) 520 0855

AutoAnalyzer Applications

Method No US- 696D-82X

Ammonia in Water and Wastewater

Range 0 010-3 mg/l N

Description

The automated procedure for the determination of ammonia utilizes the Berthelot Reaction in whi the formation of a blue colored compound believed to be closely related to indophenol occurs whe the solution of an ammonium salt is added to sodium phenoxide, followed by the addition of sodiu hypochlorite A solution of EDTA is added to the sample stream to eliminate the precipitation of th hydroxides of calcium and magnesium [1 2 3 4 5 6] Sodium nitroprusside is added to intensify the blue color

UNCONTROLLED

Hardware: Pump tubes
37°C heating bath (MT12) 7+1air+1 sampler wash

Performance data using aqueous standards

Test range 0010-3 mg/L N

	AA3	AAII
Sampling rate	40/hr	40/hr
Sample wash ratio	4 1	4/1
Sensitivity at 3mg/L	0 3576	0 22
Reagent Absorbance	0 062	0.4
Coefficient of Variation	0.429	1.2
30 replicates at 1 5mg/L		
Pooled standard deviation	0 013mg/L	NA
25 at 5 levels		
Correlation coefficient (Linear)	0 9993	NA
Detection limit	0 016	NA
(determined according to EPA procedure pt 135, app B)		
Carryover	0 2%	NA
Lag time	9 min	NA
Base	-16465	NA
Gain	24	NA
Lamp Intensity	58	NA

COPY

Note the above performance specifications were developed with the exclusive use of genuine Bran+Luebbe parts
*Trademark of Atlas Chemical

1 Van Slyke O D and Hillem A J BioChem 102 p 499 1933
2 Kallman S Presentation at Div 1 Meeting of ASTM Committee E 3 April 1967 San Diego CA
3 Bolleter W T Bushman C J and Tidwell P N Anal Chem 33 P 592 1961
4 Tellow J A and Wilson A L Analyst 89 p 453 1954
5 Tarugi A and Lenci F Boll Chim Farm 50 p 9070 1912
6 VWPCA Methods of Chem Anal of Water & Wastewater November 1969 p 137

BRAN+LUEBBE
1025 Busch Parkway Buffalo Grove IL 60089
(847) 520-0700
FAX (847) 520-0855

Reagents

Unless otherwise specified, all chemicals should be of ACS grade or equivalent

List of Raw Materials

Ammonium Sulfate $(NH_3)_2SO_4$) Primary Standard Grade
Brij-35 30% Solution*
Disodium, ethylenediamine-tetracetate
Phenol, loose crystals (C_6H_5OH)
Sodium Hydroxide (NaOH)
Sodium Hypochlorite, 5% Solution (NaOCl) Commercial Grade, e g Clorox
Sodium Nitroprusside ($Na_2Fe(CN)_5NO\ 2H_2O$)
Sulfuric Acid conc (H_2SO_4)

UNCONTROLLED

Reagent Make-Up

All water used in reagent and standard preparation must be ammonia free

Alkaline Phenol

Phenol loose crystals	83 g
Sodium Hydroxide solid	48 g
Distilled Water qs	1000 ml

COPY

Preparation
Add 83 g of loose crystal phenol to about 800 ml of distilled water While cooling under tap water or in an ice bath slowly with swirling add 48 g of sodium hydroxide Cool to room temperature dilute to 1000 ml with distilled water and mix thoroughly Store in an amber glass container This material is corrosive Stability Two weeks

Sodium Hypochlorite Solution

Sodium Hypochlorite Solution 5%	210 ml
Distilled Water qs	500 ml

Preparation
Dilute 210 ml of sodium hypochlorite solution 5% to 500 ml with distilled water and mix thoroughly Prepare fresh weekly

Sodium Nitroprusside Solution

Sodium Nitroprusside	3 5 g
Distilled Water qs	1000 ml

Preparation
Dissolve 3 5 g of sodium nitroprusside in about 600 ml of distilled water Dilute to one liter with distilled water and mix thoroughly Store in an amber container
Stability One month

BRAN+LUEBBE
1025 Busch Parkway Buffalo Grove IL 60089
(847) 520-0700
FAX (847) 520-0855

Disodium EDTA

Disodium EDTA	33 6 g
Sodium Hydroxide 50% w/w	0 8 g
Distilled Water qs	1000 ml
Brij-35	2 ml

Preparation
Dissolve approximately 0 8 g of 50% w/w sodium hydroxide and 33 6 g of disodium EDTA in about 800 ml of distilled water Dilute to one liter Add 2 ml of Brij-35 and mix well

UNCONTROLLED

Standard Preparation

Stock Standard A, 100 mg/L N

Ammonium Sulfate	0 4717 g
Chloroform	1 ml
Distilled Water qs	1000 ml

Preparation
In a one liter volumetric flask containing about 800 ml of distilled water dissolve 1 ml of chloroform Add 0 4717 g of ammonium sulfate and swirl to dissolve Dilute to one liter with distilled water and mix thoroughly

COPY

Stock Standard B 20 mg/L N

Stock Standard A	20 0 ml
Distilled Water, qs	100 ml

Preparation
Dilute 20 0 ml of stock standard A to 100 ml with distilled water and mix thoroughly Prepare fresh daily

Working Standard Solutions

ml Stock B	mg/l N
2 0	0 4
4 0	0 8
6 0	1 2
8 0	1 6
10 0	2 0
15 0	3 0

Preparation
Transfer aliquots of Stock Standard 6 as noted above to individual 100 ml volumetric flasks Dilute to volume with distilled water and mix thoroughly Prepare fresh daily

BRAN+LUEBBE
1025 Busch Parkway Buffalo Grove IL 60089
(847) 520-0700
FAX (847) 520-0855

Sample Preparation

1. Preserve by addition of 2 ml/L H_2SO_4 and refrigerate at 4° C
2. Sample turbidity should be removed by filtration prior to analysis It may interfere with this chemistry
3. Sample cups can be rinsed with 1 1 hydrochloric acid followed by distilled water and finally by an aliquot of the sample itself

System Cleansing Procedure

Pump 5N H_2SO_4 as the cleaning solution

UNCONTROLLED

System Performance

Maximum reagent/water baseline	0 40 AU
Reagent Equilibration time	5 min
Sensitivity of high standard at a STD CAL of 1 0	0 22 AU
Coefficient of Variation	1 2%

Flow Diagram

1. If analysis is to be performed in a contaminated environment scrub the air with 5N H2SO4
2. Check that the appropriate harness and optical filters are secured in their proper positions

COPY

CONSUMMABLES

The following annual consumption rates are based on system operation 8 hours/day 250 days/year

Description	Part Number	Est Annual Usage
ORN/BLU 0 05mL/min	116-0549 03	5pkg /12
ORN/YEL 0 16mL/min	116-0549 05	3pkg /12
BLK/BLK 0 32mL/min	116-0549 07	5pkg /12
ORN/ORN 0 42mL/min	116 0549 08	3pkg /12
WHT/WHT 0 60mL/min	116 0549 09	3pkg /12
GRY/GRY 1 00mL/min	116-0549 11	3pkg /12
GRN/GRN 2 00mL/min	116-0549 14	3pkg /12
Tubing air bar silicone	116 0543 01	8 ft
Tubing Kel-F 0 050 ID	171-0745 01	3 ft
Tubing Polyeth 0 015 ID	562-2002 01	3 ft
Tubing Polyeth 0 030 ID	562 2003 01	3 ft

BRAN+LUEBBE
1025 Busch Parkway Buffalo Grove IL 60089
(847) 520 0700
FAX (847) 520-0855

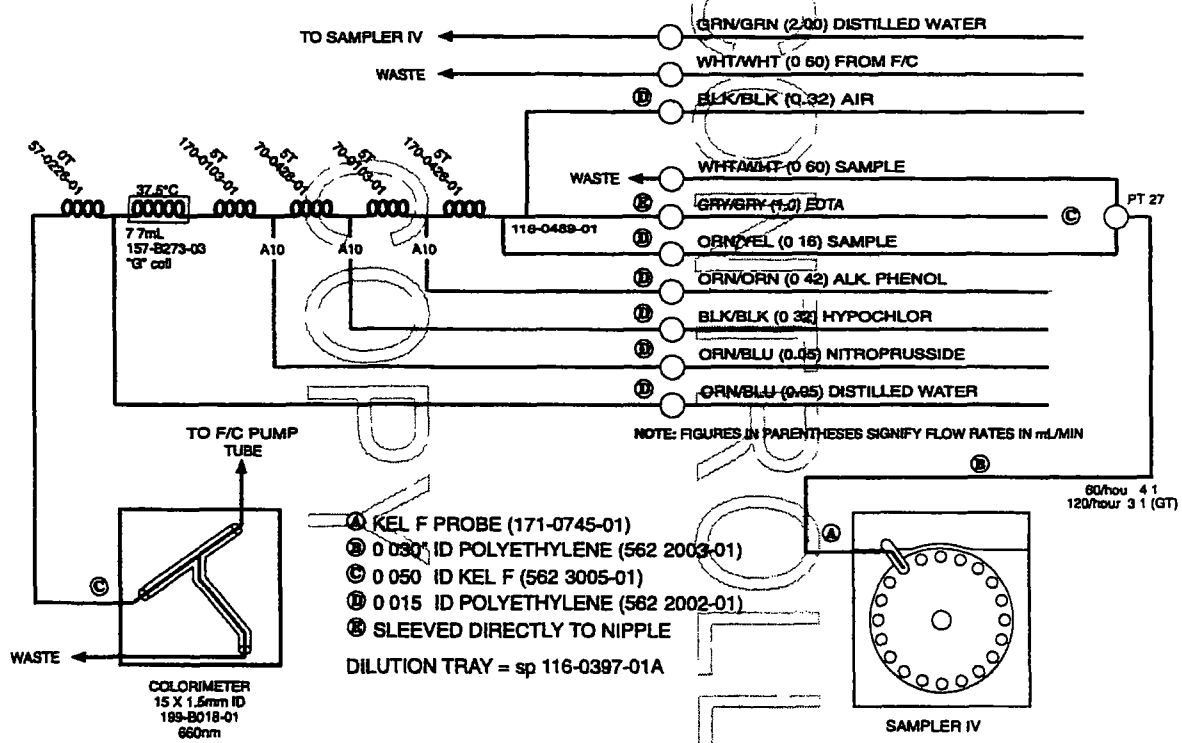
SPARES	Part Number	Recommended
AA3 Flowcell 1 5 x 10mm	169+B040-01	1pc
AAII Flowcell, 1 5 x15mm	199-B018-01	1pc
AA3 Filter 660nm	165-B044-66	1pc
AAII Filter 660nm	170-B070-26	1pc
AAII Heating Bath 7 7mL 37°C	157-B273-03	1pc
AA3 Heating Bath Coil 5 37mL	169+B440-03	1pc
5-turn mixing coil, right	170-0103-01	1pc
5-turn mixing coil left	170-0426-01	1pc
10-turn mixing coil	157-0226-01	1pc
Glass fitting, A10	116-B034-01	1pc
Injection Fitting	116-0489-01	1pc
Straight tube	116-G004-01	1pc
Glass U	172-9038-01	1pc
Glass Z	170-0204-01	1pc
Glass tube	170-G022-01	1pc
Glass tube with injection	170-G071-01	1pc

UNCONTROLLED

COPY

Method 696D-82W

Ammonia in water and wastewater
Manifold 116-D857-01
Harness number 116 B346-01
Range 0 02-3mg/L NH_3 N



4/8/94

BRAN+LUEBBE
1025 Busch Parkway Buffalo Grove IL 60089
(847) 520-0700
FAX (847) 520 0855

UNCONTROLLED

STANDARD OPERATING PROCEDURE

PHOSPHORUS DETERMINATION USING COLORIMETRIC PROCEDURE

GEN-365.3
Revision 10
August 28, 2008

UNCONTROLLED

Approved By _____ Supervisor 8/28/08 Date

_____ QA Manager 8-28-08 Date

_____ Laboratory Manager 8/28/08 Date

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso Washington 98626

© Columbia Analytical Services Inc 2008

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

PHOSPHORUS DETERMINATION USING COLORIMETRIC PROCEDURE

1 SCOPE AND APPLICATION

1 1 This procedure applies to the determination of ortho hydrolyzable and total phosphorus and is applicable to EPA method 365 3 and SM 4500P- E

1 2 The analytical procedures detailed in this SOP are applicable to most aqueous samples A preparative procedure is also described for determination of total phosphorus is soils and solids

1 3 The standard calibration range for this method is 0 to 0 7 mg/L with a 50 mm cell This range may be extended by sample dilution, or by choosing a longer or shorter path length

1 4 The standard Method Reporting Limit (MRL) for method 365 3 is currently 0 01 mg/L in solution for total and orthophosphorus and 0 05mg/L for method SM 4500P- F for orthophosphorus Method Detection Limits of 0 003 mg/L orthophosphorus (365 3) 0 02mg/L orthophosphorus (SM 4500-P- E) and 0 004 mg/L total phosphorus have been achieved The MRL in soil is 0 1 mg/kg

2 METHOD SUMMARY

2 1 Ammonium molybdate and Antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex This complex is reduced to an intensely blue-colored complex by ascorbic acid The intensity of the blue color is proportional to the phosphorus concentration

2 2 Only orthophosphate forms a blue color in this test Determination of other phosphorus forms requires a preliminary digestion step to convert other forms to orthophosphate Sample preparation procedures for phosphorus are given in section 12

3 DEFINITIONS

3 1 Total Phosphorus (P) - All of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure

3 2 Total Orthophosphate (P Ortho) - Inorganic phosphorus [$(PO_4)^{3}$] in the sample as measured by the direct colorimetric analysis procedure

3 3 Total Hydrolyzable Phosphorus (P, Hydro) - Phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure and minus pre-determined orthophosphates This hydrolyzable phosphorus includes polyphosphorus [$(P_2O_7)^{-4}$, $(P_3O_{10})^{5}$, etc] plus some organic phosphorus

3 4 Total Organic Phosphorus (P Org) - Phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure and minus hydrolyzable phosphorus and orthophosphate

3 5 Dissolved Phosphorus (P D) - All of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0 45 micron pore size and measured by the persulfate digestion procedure

UNCONTROLLED

3 6 Dissolved Orthophosphate (P-D Ortho) - As measured by the direct colorimetric analysis procedure

3 7 Dissolved Hydrolyzable Phosphorus (P-D Hydro) - As measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates

3 8 Dissolved Organic Phosphorus (P-D, Org) - As measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate

3 9 The following forms when sufficient amounts of phosphorus are present in the sample to warrant such consideration may be calculated

COPY

3 9 1 Insoluble Phosphorus (P-I) = (P) - (P-D)

3 9 2 Insoluble Orthophosphate (P-I Ortho) = (P Ortho) - (P-D Ortho)

3 9 3 Insoluble Hydrolyzable Phosphorus (P-I Hydro) = (P Hydro) - (P-D, Hydro)

3 9 4 Insoluble Organic Phosphorus (P-I, Org) = (P, Org) - (P-D Org)

4 INTERFERENCES

4 1 Arsenate is determined similarly to phosphorus and should be considered when present This interference may be eliminated by reducing the arsenic acid to arsenious acid with sodium bisulfite

4 2 When high concentrations of iron are present low recovery of phosphorus will be obtained because iron consumes a portion of the reducing agent The bisulfite treatment will also eliminate this interference

4 3 Samples with extremely high organic content may deplete the available oxidant and not digest fully with the persulfate digestion procedure These samples may require use of the Nitric/Sulfuric acid digestion found in the 18th Edition of Standard Methods for the Examination of Water and Wastewater as method #4500-P B

4 4 Samples that contain high levels of manganese may form permanganate during persulfate digestion This will be indicated by a pink color in the solution As formation of permanganate consumes some of the persulfate reaction time should be extended to allow the permanganate to complete the oxidation of organic matter

4 5 SM 4500-P E Arsenates react with the molibdate reagent to produce a blue color similar to that formed with phosphate Concentrations as low as 0 1 mg As/L interfere with the phosphate determination Hexavalent chromium and NO2- interfere to give results about 3% low at concentrations of 1 mg/L and 10 to 15% low at 10mg/L Sulfide (Na2S) and silicate do not interfere at concentrations of 1,0 and 10mg/L

5 SAFETY

5 1 All appropriate safety precautions for handling solvents reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment such as safety glasses lab coat and the correct gloves

5 2 Chemicals reagents and standards must be handled as described in the CAS safety policies approved methods and in MSDSs where available Refer to the CAS Environmental Health and Safety Manual and the appropriate MSDS prior to beginning this method

5 3 This procedure involves the use of sulfuric acid Care must be taken to prevent direct contact with concentrated these acids

6 SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6 1 Sample containers may be of plastic material or of pyrex glass Collect a minimum of 50mL of sample preferably 500 mL for liquid samples For soils, collect a minimum of 10 grams

6 2 Samples for T-Phos should be preserved by the addition of 2 ml conc H_2SO_4 per liter

6 3 Store samples in refrigerator at 4±2°C Analysis for O-Phos should be performed within 48 hours Analysis for T-Phos should be performed within 28 days There is no holding time established for soils

7 APPARATUS AND EQUIPMENT

7 1 Spectrophotometer with wavelength set to 650 nm for O-Phos and T-Phos by 365 3 and 880 nm for O-Phos by SM 4500-P- E

7 2 Acid washed 150 and 250 ml beakers 50 and 100 ml graduated cylinders and class A pipettes

7 3 Calibrated Eppendorf/MLA/Oxford pipettors and tips

7 4 Hot plate for digestions and bisulfite treatment

7 5 Analytical balance - capable of weighing to the nearest 0 0001 g

7 6 Top-loader balance - capable of weighing to the nearest 0 01 g

8 REAGENTS

8 1 Method SM 4500-P E

8 1 1 Sulfuric acid H2SO4 5N Dilute 70ml conc H2SO4 to 500ml with distilled water

8 1 2 Potassium antimonyl tartrate solution Dissolve 1 3715 g K(SbO)C4H4O6 1/2H2O in 400ml distilled water in a 500 ml volumetric flask and dilute to volume. Store in a glass-stoppered bottle

8 1 3 Ammonium molybdate solution Dissolved 20 g (NH4)6Mo7O24 4H2O in 500 ml distilled water Store in a glass-stoppered bottle

8 1 4 Ascorbic acid 0 1M Dissolve 1 76 g of ascorbic acid in 100 ml of distilled water This solution is stable for 1 week

8 1 5 Combined reagent Mix the above reagents in the following proportions for 100 mm of the combined reagent 50ml 5N H2SO4 5 ml potassium antimonyl tartrate solution 15 ml ammonium molybdate solution and 30ml ascorbic acid solution Mix after addition of each reagent Let all reagents reach room temperature before they are mixed and mix in the order given If turbidity forms in the combined reagent Shake and let stand for a few minutes until turbidity disappears before proceeding Thee reagent is stable for 4 h

8 2 Method 365 3

8 2 1 Ammonium molybdate-antimony potassium tartrate solution Dissolve 8 g of ammonium molybdate and 0 2 g antimony potassium tartrate in 800 ml of distilled water and dilute to 1 L This reagent expires 6 months from date of preparation

8 2 2 Ascorbic acid solution Dissolve 60 g of ascorbic acid in 800 ml of distilled water and dilute to 1 L Add 2 ml of acetone This solution is stable for two weeks

8 2 3 Sulfuric acid 11 N - Slowly add 310 ml of concentrated H_2SO_4 to approximately 600 ml distilled water Cool and dilute to 1 liter This reagent expires 6 months from date of preparation

8 2 4 Sodium bisulfite ($NaHSO_3$) solution Dissolve 5 2 g of $NaHSO_3$ in 100 ml of 1.0 N H_2SO_4 This reagent expires 6 months from date of preparation

8 2 5 Ammonium persulfate, crystals - ACS Grade This chemical expires 5 years from date opened

8 2 6 Stock phosphorus solution Dissolve 0 2196 g of predried (105°C for one hour) KH_2PO_4 in distilled water and dilute to 500 ml 100 mg/L P This standard expires 6 months from date of preparation

8 2 7 Organic Phosphorus Spike (100 µg/ml - P) for total phosphorus Dissolve 0 1180 g of Adenosine mono-phosphate (AMP) in DI water and dilute to the mark in a 100 ml class A volumetric flask This reagent expires 6 months from date of preparation

8 2 8 All prepared reagents have an expiration period of one year unless otherwise specified

8 2 9 Reagent water laboratory deionized water

9 RESPONSIBILITIES

9 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

9 2 It is the responsibility of the department supervisor/manager to document analyst training Documenting method proficiency as described in the SOP for Documentation of Training is also the responsibility of the department supervisor/manager

10 PREVENTIVE MAINTENANCE

No preventive maintenance is required other than normal glassware and apparatus cleaning

11 PROCEDURE

11 1 Wash all glassware with 50% HCl and hot water followed by DI

11 2 If total or hydrolyzable phosphorus is to be determined digest the samples as described below

11 2 1 Total Phosphorus

UNCONTROLLED

11 2 1 1 Add 100 ml of sample* to a 150 ml beaker along with 2 ml of 11 N H_2SO_4 and ≈0 8 g of Ammonium Persulfate and several glass beads Cover the beaker with a watch glass Repeat for all remaining field and QC samples

*For preparation of solid samples, place 10 g of sample and 100 mL of reagent water in the beaker and mix prior to adding the H_2SO_4 and Ammonium Persulfate

COPY

11 2 1 2 Place the covered beakers containing the sample on a hot plate, and digest for 1-2 hours or until a final volume of 20-30 ml is reached

11 2 1 3 Allow the digested samples to cool If a precipitate forms add additional DI and heat gently to dissolve If the crystals do not dissolve or if the digestate contains sediment filter the digestate through a 0 45 µm filter and collect the filtrate in a beaker if the bisulfite treatment is required, or a 100 ml volumetric flask or equivalent container if no bisulfite treatment is needed

11 2 1 4 If the digestate is colored or if metal ion interferences are suspected treat the samples and standards by adding 10 ml of sodium bisulfite solution per 100 mls of sample and warming gently for approximately 30 minutes Routine use of the bisulfite treatment is strongly advised The sodium bisulfite treatment is most effective after filtering sample through a 0 45µm filter

11 2 1 5 Transfer the digestate to a 100 ml volumetric flask or equivalent container, and dilute to the mark with DI

11 2 2 Hydrolyzable phosphorus

11 2 2 1 Add 1 ml of H2SO4 solution (8 3) to a 50 ml sample in a 125 ml Erlenmeyer flask

11 2 2 2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached Do not allow sample to go to dryness Alternatively heat for 30 minutes in an autoclave at 121°C (15-20 psi) Cool dilute to approximately 40 ml and filter

11 2 2 3 Treat the samples as in 11 2 1 4 and 11 2 1 5 above

11 3 Prepare a series of standards according to the following table Be certain to use class A volumetric glassware, and properly calibrated Eppendorf/MLA pipettors An undeveloped standard curve is stable for one week

Volume of 100 mg/L O-Phos Standard (mL)	Final Volume (mL)	Standard Conc (mg/L)
0	100	0 00
0 01	100	0 01
0 05	100	0 05
0 10	100	0 10
0 20	100	0 20
0 50	100	0 50
0 70		0 70

Note This standard curve expires one week from date of preparation For method SM 4500-P E do not make the 0 01 mg/L Standard

11 4 Calibration of Spectrophotometer

11 4 1 O-Phos and T-Phos (365 3) Transfer 50 ml of each standard into a 150 ml beaker add 1 ml of 11 N sulfuric acid and 4 ml of molybdate-antimony potassium tartrate and mix Add 2 ml of ascorbic acid reagent mix, and allow to sit for five minutes to allow for full color development

11 4 2 O-Phos (SM 4500-P E) Pipet 50ml standard into a clean dry 150 ml beaker Add 8 0 ml combined reagent and mix thoroughly After at least 10 min but no more than 30 min measure absorbance of each standard at 880 nm using reagent water as the reference solution

11 4 3 The calibration curve is fitted to a linear least squares model See Appendix A Set the spectrophotometer to 650 nm for 365 3 and 880 nm for SM 4500-P E and zero with DI water Read the standards calculate the correlation coefficient slope

and intercept The correlation coefficient must be ≥ 0 995 If the calibration criteria are met analyze an LCS If the LCS recovery is acceptable proceed with analysis of samples If not determine the cause of the problem, correct it, and then recalibrate

11 4 4 Analyze an ICB (a 0 0 mg/L standard) The result must be less than the reporting limit

11 4 5 To verify spectrophotometer calibration analyze an ICV for T-Phos at a concentration of 0 4 mg/L The result must be within 10% of the true value

11 5 Analysis of Samples

11 5 1 365 3 Method Highly colored or turbid samples may require background correction To do this, add 1 1 N sulfuric acid and Ammonium molybdate-antimony potassium tartrate reagent to a separate aliquot of sample, and read the absorbance Subtract this absorbance from that of the sample with all reagents added, prior to final calculation If the background is greater than 0 2-0 3 absorbance units, or greater than the sample aliquot with all reagents added, dilute the sample and redetermine the background color Some highly turbid samples may require filtration to remove suspended matter

11 5 2 SM 4500-P E Method Highly colored or turbid samples may require background correction To do this, add all reagents except ascorbic acid and potassium antimonyl tartrate and read the absorbance Subtract this absorbance from that of the sample with all reagents added, prior to final calculation

11 5 3 Samples with high levels of arsenate iron or manganese should be treated with sodium bisulfite prior to analysis See method 365 3 for the proper procedure Note that the bisulfite treatment should follow any filtration performed on the samples as interfering substances may dissolve from any sediment present

11 5 4 For 365 3 Transfer 50 ml of sample to a 150 ml beaker and develop color as specified in 12 4 1 for the standards except that no additional acid is added to samples that have been digested for total or hydrolyzable phosphorus

11 5 5 For O-Phos by SM 4500 P E transfer 50 ml of sample to a 150 ml beaker and add 0 05ml (1 drop) phenolphthalein indicator If red color develops add 5N H_2SO_4 solution dropwise to just discharge the color Add 8 0 ml combined reagent and mix thoroughly After at least 10 min but no more than 30 min measure absorbance of each standard at 880 nm using reagent water as the reference solution

11 5 6 If sample absorbance exceeds the highest standard dilute a suitable portion of sample to 50 ml and proceed with color development and analysis If a dilution is

performed add additional acid to total or hydrolyzable phosphorus samples to ensure that each 50 ml aliquot of diluted sample contains 1 ml of 11 N H_2SO_4

12 QA/QC REQUIREMENTS

12 1 The ability of each analyst/instrument to generate acceptable accuracy and precision must be documented prior to sample analysis by performing 4 replicate LCS analyses and calculating average recovery and %RSD Method criteria must be met for these results This must be completed before analysis of samples or whenever significant changes to the procedures have been made

12 2 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. The MDL studies should be done for each matrix, prep method and instrument Refer to the CAS SOP for The Determination of Method Detection Limits and Limits of Detection

12 3 Ongoing QC Samples required for each sample batch (20 or fewer samples) are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches In general these include

12 3 1 Method blanks - Method Blanks are aliquots of reagent water which are carried through the same procedure as the samples Method Blanks must not contain detectable amounts of analyte > MRL or the samples must be rerun

12 4 The LCS or laboratory control standard is a purchased standard used to check the performance of the analytical system The LCS recovery must be within acceptance limits before samples can be analyzed

12 4 1 CCV's are portions of 0 5 mg/L standard which are analyzed to verify continued spectrophotometer calibration CCV's must be within 10% of the true value (96-104% for Arizona samples) or the affected sample batch must be repeated

12 4 2 CCB's are 0 0 mg/L standards CCB's must be less than the reporting limit or the affected batch must be repeated

12 4 3 Matrix duplicates and matrix spikes must be run at a minimum of one set per batch of 20 or fewer samples CCV/CCB pairs must be run after every 10th reading made on the spectrophotometer

12 4 4 The relative percent difference (RPD) between matrix duplicates should be within acceptance limits If not the supervisor should be notified at the time of analysis, and corrective action taken as appropriate for the sample

12 4 5 Matrix spike recovery must be within acceptance limits If not the sample must be checked for interferences and reanalyzed Samples should be spiked at ~5 times the expected sample value Spike levels may be calculated as follows

Aqueous matrices

$$Spike\ added = \frac{spike\ concentraction\ (mg\ /L\ )\ x\ volume\ of\ spike\ taken\ (ml\ )}{ml\ of\ sample\ used}$$

Nonaqueous matrices

$$Spike\ added = \frac{spike\ concentration\ (mg/L)\ x\ volume\ of\ spike\ taken\ (ml)}{g\ of\ sample\ used\ x\ \%solids(if\ applicable)}$$

Calculate percent recovery as follows

$$Matrix\ Spike\ Recovery = \frac{Spiked\ Sample\ -\ Sample}{Spike\ Added}\ x\ 100$$

QC Acceptance Limits						
Parameter	LCS (% Recovery)		MS (% Recovery)		RPD (%)	
	Water	Soil	Water	Soil	Water	Soil
Total Phosphorus	85-115[d]	85-115[i]	75-125[d]	75-125[i]	20[d]	20[d]
Ortho Phosphorus	85-115[d]	-	75-125[d]	-	20[d]	20[d]

[d] Default limits which are within laboratory statistical limits

[i] Default limits – insufficient data points for determination of laboratory statistical limits

13 DATA REDUCTION AND REPORTING

13 1 All data and corrective actions must be recorded into the bench records by the analyst All analysis descriptions (samples blanks CCVs etc), measurements, and readings are recorded on the applicable benchsheet The benchheet is used to document all analyses and to perform calculations leading for final sample results

13 2 It is the analyst s responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run Results for QC analyses are calculated and recorded as specified for samples These results are then used to calculate QC determinations (recovery RPD etc)

13 3 Following sample and QC analyses calculate results as follows

Water matrices

$$mg/L\ P = \frac{mg/L\ \ standard\ curve\ x\ final volume(mL)}{Initial\ sample\ volume(mL)}$$

$$Spike\ added = \frac{spike\ concentration(mg/L)\ x\ volume\ of\ spike\ taken(ml)}{ml\ of\ sample\ used}$$

Nonaqueous matrices

$$mg/kg\ P = \frac{(mg/L\ \ curve)(Final\ Solution\ Volume)}{(Sample\ Weight\ g)(\%\ Solids)}$$

$$Spike\ Added = \frac{(Spike\ Solution\ Concentrated(mg/L))(Volume\ of\ Spike\ Added(ml))}{(Sample\ Weight\ g)(\%\ Solids)}$$

13 4 The data packet for the sequence is submitted for review by supervisor or designee The results are transferred to the appropriate report form located in the CAS network directory R \WET\WIP These forms are made from templates located in R \WET\FORMS Once the results are transferred the report is reviewed

13 5 Reporting results as Orthophosphate as Phosphorus in mg/L or mg/kg units or for total phosphorus 'Phosphorus Total in mg/L or mg/kg units

13 6 Refer to the SOP for Laboratory Data Review Process for general instructions for data review

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also refer to the *SOP for Corrective Action* for correct procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the *SOP for Report Generation* or in project specific requirements

15 METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

The method detection limit (MDL) is established using the procedure described in the *SOP for The Determination of Method Detection Limits and Limits of Detection* (ADM-MDL) Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual

UNCONTROLLED

16 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound feasibly possible and within method requirements Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly

17 WASTE MANAGEMENT

COPY

17 1 The laboratory will comply with all Federal State and local regulations governing waste management particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual

17 2 This method uses acid Waste acid is hazardous to the sewer system and to the environment All acid waste must be neutralized to a pH of 2 5-12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record See the CAS EH&S Manual for details

17 3 This method uses a base Waste base is hazardous to the sewer system and to the environment All waste must be neutralized to a pH of 2 5-12 prior to disposal down the drain The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record See the CAS EH&S Manual for details

18 TRAINING

18 1 Refer to the *SOP for Documentation of Training* for standard procedures

18 2 Training outline

18 2 1 Review literature (see references section) Read and understand the SOP Also review the applicable MSDS for all reagents and standards used Following these reviews observe the procedure as performed by an experienced analyst at least three times

18 2 2 The next training step is to assist in the procedure under the guidance of an experienced analyst During this period the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst

18 2 3 Perform initial precision and recovery (IPR) study as described above for water samples Summaries of the IPR are reviewed and signed by the supervisor Copies may be forwarded to the employee s training file For applicable tests IPR studies should be performed in order to be equivalent to NELAC s Initial Demonstration of Capability

18 3 Training is documented following the *SOP for Documentation of Training*

NOTE When the analyst training is documented by the supervisor on internal training documentation forms the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently

19 REFERENCES

19 1 EPA Method 365 3

19 2 Method 4500-P E in Standard Method for the Examination of Water and Wastewater, 20th Ed 1998

APPENDIX A

The calibration is determined using a linear regression that best fits the line of the X Y pairs The quality of the fit is determined by calculating the coefficient of determination (R^2) also called the correlation coefficient

The line of regression is calculated as follows

Start with the equation for a line y = mx + b From here the line of regression can be determined

UNCONTROLLED

$$m = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - \left(\sum x\right)^2}$$

$$b = \frac{\sum y - m\sum x}{n}$$

COPY

Where

x = the values of the x variables
y = the values of the y variables
n = the number of data points

Once the line of regression has been determined then the coefficient of determination can be calculated

$$r^2 = \frac{\left(\sum xy - n\bar{x}\bar{y}\right)^2}{\left(\sum x^2 - \bar{x}\sum x\right) * \left(\sum y^2 - \bar{y}\sum y\right)}$$

STANDARD OPERATING PROCEDURE

LABORATORY BALANCE MONITORING AND CALIBRATION

ADM-BAL
Revision 1
August 7, 2008

UNCONTROLLED

Approved By _____ QA Manager, 8-7-08 Date

_____ Laboratory Director, 8/7/08 Date

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2008

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

LABORATORY BALANCE MONITORING AND CALIBRATION

1 PURPOSE

This SOP provides instructions for performing routine monitoring and calibration of laboratory balances This is required in order to ensure proper operation of this equipment and to document compliance with QA program requirements

2 APPLICABILITY

UNCONTROLLED

This procedure applies to all balances used throughout the lab for any type of sample, standard reagent, or miscellaneous weighing

3 RESPONSIBILITIES

3 1 Balance calibration verifications are performed by the department staff where the balances are located and used It is the responsibility of the department manager and supervisor to ensure that the balance calibration verifications are performed as specified in this SOP

COPY

3 2 Laboratory QA staff is responsible for coordinating periodic outside service, calibration, and cleaning Laboratory QA staff is responsible for reviewing and maintaining the outside service certificates

3 3 Laboratory QA staff is responsible for providing departments with calibrated reference weights Laboratory QA staff is responsible for coordinating periodic outside calibration of the weights and reviewing/maintaining the calibration certificates

4 APPARATUS

Reference weights – Troemner (or equivalent) 1,10, 100, 300, and 1000g, ASTM Class 2 (or Class1) or NIST Class S Calibration is verified annually by outside metrology service Depending on the balances in use in various departments, sets of weights are made to accommodate balance operating ranges

5 PROCEDURE

5 1 Balance calibration verifications are required for each day the balance is used The NELAC Quality System Standards and DoD Quality System Manual require that the balance verifications be performed *prior to use* on each day of use The calibration verification weights must bracket the range of use

5 2 A bound logbook is used to record all measurements Format the logbook such that the date, initials balance I D , measurements, and specifications (for the 3 weights) are listed for each balance Record each calibration verification in the logbook

5 3 Measurement Procedures

5 3 1 Brush off the balance pan with a clean brush and check the bubble level to insure balance is leveled

5 3 2 Press the zero (tare) bar on the balance, make sure readout indicates balance is tared (reads zero)

UNCONTROLLED

5 3 3 Measure and record the three weights designated for the balance capacity and use as listed in the logbook

5 3 4 Record each measurement in the logbook, being careful to correctly identify the balance being monitored

5 3 5 Remove each weight and re-zero before performing the next measurement

5 3 6 The criteria for the weights being measured is as follows

COPY

Analytical balances	±0 1% or ±0 5mg, whichever is larger*
Top-loading balances	±0 1% **

* Unless method-specific guidance exists
** ASTM D 4753

5 4 Corrective Action for out-of-control events

5 4 1 An out-of-control situation occurs when a measurement falls outside of specific criteria If a balance yields a measurement that is out-of-control, several steps may be taken to return the instrument to control Initially, the technician should review recent measurements taken from the balance, and inspect the equipment to insure that it is properly functioning It is very important to check the bubble-level located on the balance to ensure that the balance is properly leveled

5 4 2 If inspection and/or minor adjustment of the balance do not result in a return to control the balance should be temporarily taken out of service, either by physical removal or by disconnecting the power to the balance and identifying it as being temporarily unavailable for use The vendor responsible for routine metrological

services should be notified and the situation described, if return to control can be accomplished with remote instruction this is acceptable

5 4 3 If the balance requires service from the vendor all necessary paperwork should be performed and the balance delivered to the service vendor, preferably by CAS courier, if possible Where sample results are jeopardized, a non-conformity and corrective action report (NCAR) should be written and reviewed by the Quality Assurance Manager, and a copy placed in the file containing all appropriate balance information

6 RECORDS

UNCONTROLLED

6 1 All measurements are to be recorded in the applicable logbook as described above. Entries into logbooks are to be performed in accordance with the *SOP for Making Entries into Logbooks and Onto Benchsheets* (ADM-DATANTRY)

6 2 All certificates of calibration provided by outside calibration service contractors will be reviewed by the QA Manager

7 REFERENCES

COPY

7 1 NELAC Quality Standards 2003

7 2 CAS-Kelso Quality Assurance Manual

7 3 Department of Defense Quality Systems Manual for Environmental Laboratories Version 3, January 2006

8 CHANGES FROM PREVIOUS REVISION

8 1 Section 5 3 6, replaced previous criteria with criteria based on analytical balance or top-loader, as per DoD QSM Added ASTM reference

8 2 Section 7, added ASTM reference

8 3 Attached ASTM D4753

ATTACHMENT

ASTM D4753

UNCONTROLLED

COPY

Designation D 4753 – 87

Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing[1]

This standard is issued under the fixed designation D 4753 the number immediately following the designation indicates the year of original adoption or in the case of revision the year of last revision A number in parentheses indicates the year of last reapproval A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval

1 Scope

1 1 This specification provides minimum requirements for general purpose scales balances and standard masses used in soil and rock testing

1 2 This specification provides guidance for evaluating selecting and specifying general purpose scales balances and standard masses used in soil and rock testing

1 3 The accuracy requirements for balances and scales are specified in terms of the combined effect of all sources of error contributing to overall balance performance The measurement of specific sources of error and consideration of details pertaining to balance construction have been intentionally avoided

1 4 This specification does not include requirements for balances and scales that have accuracies greater than those generally required in normal soil and rock testing

1 5 This specification does not apply to nongraduated balances

1 6 This specification does not address the methods used to verify or quantify specific parameters dealing with balances and scales For a description of tests used in evaluating balance performance see NBS Handbook 44

1 7 This specification is not intended to be used as a specification for the purchase of balances and scales

NOTE 1—The National Bureau of Standards (NBS) and the International Organization of Legal Metrology (OIML) publish standards or practices that specify construction requirements as well as performance specifications for balances ASTM OIML, and NBS publish construction standards and tolerances for standard masses

NOTE 2—The terms "mass" and "determine the mass of" are used in this standard instead of the more commonly used terms "weight" and "weigh" to comply with standard metric practice In addition the term "standard mass(es)" is used instead of "weight(s) when referring to a piece of material of known specified mass used to compare or measure the mass of other masses

2 Referenced Documents

2 1 *ASTM Standard*

E 617 Specification for Laboratory Weights and Precision Mass Standards[2]

2 2 *National Bureau of Standards Documents*

NBS Handbook 44 Specifications Tolerances and Other Technical Requirements for Weighing and Measuring Devices[3]

NBS Handbook 105 1 Specifications and Tolerances for Reference Standards and Field Standard Weights and Measures[3]

2 3 *International Organization for Legal Metrology (OIML)*

International Recommendation No 20 Weights of Accuracy Classes E_1 E_2 F_1 F_2 M_1 from 50 kg to 1 mg[4]

International Recommendation No 3

3 Descriptions of Terms Specific to This Standard

3 1 *accurate*—a balance is accurate when its performance (its indication as determined by tests made with suitable standards) conforms to the standard within the applicable tolerances and other performance requirements Balances that fail to conform are inaccurate

3 2 *balance*—an instrument for determining the mass of an object by the action of gravity on the object See *scale*

NOTE 3—In this specification the terms balance and scale are used interchangeably as is often done The term balance is more often used in scientific fields of application See Note 7

3 3 *basic condition*—a basic condition is a condition that must be met before a basic measurement for evaluating a balance can be performed

3 4 *basic measurement (of error)*—a basic measurement for evaluating a balance is performed by (*1*) determining the change of indication of the balance when a load of known mass is added to or subtracted from any load already on the balance and (*2*) taking the difference between the change in the indication determined and the known value of the mass

3 5 *basic tolerance*—basic tolerances are those tolerances that are established by a particular code for a particular device under all normal tests whether maintenance or acceptance Basic tolerances include minimum tolerance values when these are specified Special tolerances identified as such and pertaining to special tests are not basic tolerances

3 6 *capacity—of a balance* the maximum load recommended by the manufacturer disregarding any additional capability supplied by a taring device

3 7 *general purpose balance*—any balance used to make a general purpose determination of mass See *general purpose determination of mass*

UNCONTROLLED COPY

[1] This specification is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18 99 on Quality Control

Current edition approved Nov 27 1987 Published January 1988

[2] *Annual Book of ASTM Standards* Vol 14 02

[3] Available from the Superintendent of Documents, US Government Printing Office Washington DC 20402

[4] Available from the International Standards National Bureau of Standards, US Department of Commerce Gaithersburg MD 20899

3 8 *general purpose determination of mass*—a single determination of mass using a balance (not a special purpose determination of mass involving repeat determinations of mass averages standard deviations corrections etc)

3 9 *general purpose standard mass*—a standard mass used with a balance to make a general purpose determination of mass See *general purpose determination of mass*

3 10 *hysteresis*—the difference between indications obtained when the value of the applied load is reached by adding mass or by removing mass from the load receiving element of a balance

3 11 *linearity error*—plus or minus deviation from the theoretically straight lined (linear) course of two interdependent values In balances this expression is applied to the plus or minus deviation of the indicated measurement value from the true (actual) value of the load

NOTE 4—The term linearity implies that the deviation from the true values are a continuous function of the applied load Thus, obtaining enough values of the true applied load versus balance reading to establish a relation between applied load and output should give the error that will occur at any applied load Linearity then is a statement about the systematic (nonrandom) error of a balance Superimposed on the linearity are precision and other effects such as off-center errors, temperature effects etc Linearity is a measure of balance performance over its full range and on most balances adjustments can be made to alter the useableness of a balance with a given linearity for weighings within a particular range of use

3 12 *nongraduated balance*—balances not fitted with a scale numbered in units of mass

3 13 *off center error—of a top loading or platform balance* the difference in indicated value when a mass is shifted to various positions on the loading area (pan or platform), eccentric load error

NOTE 5—The test for off-center error is called the shift test or off-center load test Information about balance performance under eccentric loadings is not normally found in product literature but such information can usually be obtained by contacting the manufacturers directly

3 14 *precision of a balance*—the degree of agreement between the indications of a balance for repeated determinations of mass of the same mass under essentially the same conditions It is usually expressed quantitatively as a standard deviation of a series of weighings or as a function of the range of several determinations of mass See *repeatability type II reproducibility*

3 15 *readability type I*—the value of the smallest unit of mass that can be read without estimation over the given range of measurement either directly or by use of a vernier or micrometer

3 16 *readability type II*—the value of the smallest unit of mass that can be read *with* estimation over the given range of measurement

3 17 *readability type III*—the value of the smallest unit of mass that can be read while the balance is in use but not smaller than readability Type I

NOTE 6—Readability Type III refers to the smallest unit of mass that can be read when in service conditions such as draft vibration and other environmental conditions affect the balance

3 18 *repeatability type I*—the degree of agreement between the indications of a balance for repeated determinations of the same mass under essentially the same conditions The degree of agreement (qualitatively)

3 19 *repeatability type II*—see *precision*

3 20 *reproducibility*—see *precision*

3 21 *scale*—see *balance*

NOTE 7—The term scale usually refers to instruments intended for commercial or industrial applications and when so used usually implies an instrument of lesser performance than a balance

3 22 *sensitivity*—the ratio of the deflection (ΔL) of the balance indicator or self indicating display to the load (ΔM) causing the deflection $S = \Delta L/\Delta M$ at a given load

NOTE 8—Values for sensitivity are sometimes seen expressed in terms of mass units When used in this way in reference to a non self indicating balance sensitivity refers to the reciprocal of sensitivity or the change in mass required to change the position of equilibrium (rest point) a specified amount usually one division on the balance indicator When used in reference to self indicating balances it refers to the change in mass required to change the indication by one scale division

3 23 *standard mass*—an object of specified mass and construction used with balances and for the verification of balances and other masses

3 24 *taring range*—a range within which it is possible to reset the display to zero by means of the tare device

3 25 *tolerance*—a value fixing the limit of allowable error or departure from true performance or value

NOTE 9—For additional terms used in this specification related to balances and standard masses see NBS Handbook 44 or OIML IR No 3

4 Significance and Use

4 1 This specification provides those writing and using test standards related to soil and rock with a means for determining the balance capabilities required for a particular test method and for describing the balance selected in a uniform fashion

4 2 This specification provides agencies conducting soil and rock testing with guidance for selecting and evaluating general purpose balances and standard masses

4 3 This specification provides inspection organizations with criteria for evaluating general purpose balances and standard masses

5 Requirements for General Purpose Balances

5 1 General purpose balances shall be judged accurate for a given class if their indications meet the basic tolerances shown in Table 1

6 Requirements for General-Purpose Weights

6 1 General purpose standard masses for use in testing of soil and rock should conform to the requirements in Specification E 617 for Type I or Type II Grade S O or P standard masses and have tolerance limits equal to or better than those for Class 6 standard masses except that the maintenance tolerances given in Specification E 617 for Class 6 standard masses are to be considered acceptance tolerances for purposes of this specification and the maintenance tolerances twice those values The tolerances given in Table 2 correspond to the minimum acceptable maintenance tolerances under this specification

UNCONTROLLED COPY

TABLE 1 Requirements for General Purpose Balances

Class	Test Mass [A] g	Basic Tolerance	Readability Type I [B] g
GP1	≥20	±0 1 %	0 01
	<20	±0 02 g	0 01
GP2	≥200	±0 1 %	0 1
	<200	±0 2 g	0 1
GP5	≥2000	±0 1 %	1
	<2000	±2 g	1
GP10	≥5000	±0 1 %	5
	<5000	±5 g	5
GP100	≥50 000	±0 1 %	50
	<50 000	±50 g	50

[A] The known mass which is added to or subtracted from any load already on the balance when making a basic measurement (of error)
[B] Not readability Type II

NOTE 10—Former NBS Class J M S S-1 P and Q standard masses meet this specification as do OIML Class M_1 standard masses (IR No 20)

7 Evaluation of General-Purpose Balances

7 1 *Basic Tolerance*—Table 1 shows the basic tolerances for all classes of general-purpose balances used in soil or rock testing that are covered by this specification The basic tolerances shown apply to basic measurements made when evaluating a balance

7 1 1 A basic measurement for evaluating a balance is performed by determining the change of indication of the balance when a known mass is added to or subtracted from any load already on the balance and then taking the difference between the change in the indication determined and the known value of the mass To evaluate a balance, the basic tolerances shown in Table 1 are applied to the known value of the mass used in the basic measurement The result of a basic measurement must fall within the error allowed by the basic tolerance

NOTE 11—For nearly all determinations of mass encountered in soils testing, the value of interest is the difference between two determinations of mass In cases where the difference between the two determinations of mass is small relative to the total masses determined it is desirable to specify a tolerance based on the difference between the two determinations of mass to relieve what might otherwise be an excessively stringent tolerance

NOTE 12—A no load condition may be treated as a load of 0 0 g and may be considered a load on the balance

7 1 2 The basic tolerance for a balance should apply to all values of loading within the range of the balance without regard to whether the balance is properly zeroed or a tare mass is being used and should apply under all usual and customary methods of operation Furthermore the basic tolerance must be met in the environment in which the balance is to be used

7 1 3 A balance shall not be considered acceptable if the result of basic measurements involving any combination of poise locations counterpoise masses pan loading, and scale positions or unit masses are not within the basic tolerances shown in Table 1

7 1 4 When evaluating top loading balances results of basic measurements under off center loading must also meet basic tolerances

NOTE 13—The possibility of off-center error and linearity error should be considered when making basic measurements

TABLE 2 Tolerances for General Purpose Standard Masses

Denomination	Tolerance [A] mg
20 kg	4000
10 kg	2000
5 kg	1000
3 kg	600
2 kg	400
1 kg	200
500 g	100
300 g	60
200 g	40
100 g	20
50 g	14
30 g	10
20 g	6
10 g	4
5 g	4
3 g	4
2 g	4
1 g	4
500 mg	2
300 mg	2
200 mg	2
100 mg	2

[A] Acceptance tolerances on new general-purpose standard masses are one-half the maintenance tolerances shown in this table

UNCONTROLLED COPY

7 1 5 Standard masses meeting or exceeding the requirements given in Specification E 617 for weights of Type I or Type II Grades S or O and Class 2 are suggested in Specification E 617 for use as working standards for calibration and precision analytical work and are recommended in this specification for use in evaluating general purpose balances The use of standard masses of lesser quality for calibration purposes is discouraged because of the tendency to think of them as accurate once they are labeled "standard masses for calibration"

7 2 *Balance Classification*—A balance is classified by reference to its readability Type I (see Table 1)

NOTE 14—Capacity is not to be considered when classifying a balance Balance classification in this specification is based on balance performance not on use requirements When selecting a balance the anticipated loads which the balance is expected to measure will dictate the capacity required

7 3 *Basic Conditions*—A basic condition is a condition which must be met before a basic measurement for evaluating a balance can be performed In general basic conditions require that a balance give a clear and stable indication under any condition of loading including the indication at no load Both the useable readability (readability Type III) and the repeatability Type I must be adequate to perform the basic measurements described in 7 1

NOTE 15—For example when a determination of mass is made with a beam balance if the smallest poise is moved by an amount equal to the readability Type I the indicating pointer must move clearly off balance (usually at least one division on the pointer scale) This is an indication of the adequacy of the sensitivity of a balance

7 3 1 Readability Type I (not Type II) establishes the balance s class for determining the appropriate basic tolerance If environmental or other factors cause the usable readability (readability Type III) to be poorer than the readability Type I then the balance cannot meet the basic tolerance for its class

7 3 2 The repeatability Type I of the balance being evaluated must be such that the difference between the

highest and lowest values in a group of several determinations of mass of the same load shall not be greater than twice the balance s readability Type I

7 4 *Balance Testing*—Three types of testing may be performed when evaluating the performance of a balance

7 4 1 *Acceptance Testing*—Acceptance testing should be performed on new or newly repaired or reconditioned balances The basic measurement for evaluating a balance is performed in an environment that meets the manufacturer s recommendations An acceptance tolerance equal to or better than one half the basic tolerance should apply to all basic measurements for this test

7 4 2 *Maintenance Testing*—Maintenance testing should be performed on balances in service The basic measurement for evaluating a balance is performed in an environment that meets the manufacturer s recommendations Maintenance testing is performed to determine whether a balance should be repaired A tolerance equal to or better than the basic tolerance should apply to all basic measurements for this test

7 4 3 *In-Use Testing*—In-use testing should be performed on balances in service The basic measurement for evaluating a balance should be performed as and where the balance is used to make general purpose determinations of mass In use tests are intended to indicate the quality of usual and customary mass determinations that are made or may be made when using a general purpose balance The basic tolerance should apply to basic measurements for this test

7 5 *Rejection*—If a balance fails when in use tests are performed then maintenance tests should be performed If a balance fails both in use and maintenance tests, it should be removed from service and repaired or replaced If a balance fails the in use test but passes the maintenance test the environment in which the balance is located must be improved

UNCONTROLLED COPY

8 Evaluation of General Purpose Standard Masses

8 1 General purpose standard masses should be tested on a precision balance Standard masses meeting or exceeding the requirements given in Specification E 617 for standard masses of Type I or Type II Grades S or O and Class 2 are suggested in Specification E 617 for use as working standards for calibration and precision analytical work and are recommended in this specification for use in evaluating general purpose standard masses The use of standard masses of lesser quality for calibration purposes is discouraged because of the tendency to think of them as accurate once they are labeled standard masses for calibration "

8 2 General purpose standard masses that fail to meet the requirements specified in Section 6 should be removed from service and either adjusted to meet acceptance tolerances or replaced

9 Selecting and Specifying Balances

9 1 *Selecting Balances*—The selection of a balance is based on the proposed use A balance must have a capacity sufficient to accommodate all anticipated test loads and its performance must be good enough so as not to be a cause of test error The accuracy desired in test results should be used to establish the allowable balance tolerances

9 1 1 The precision of a balance (a term frequently found in manufacturer's specifications) expressed as a standard deviation, shall not be greater than one-half the readability Type I (not Type II)

9 1 2 When listed by the manufacturer, the linearity error of a balance shall not be greater than one half the readability Type I (not Type II)

9 1 3 If the maximum error of indication contributed by off-center loading can be obtained from the manufacturer it should be no greater than one half the readability Type I (not Type II)

9 1 4 In cases where a test requires that more than one test result be determined, several balances having different capabilities may be required.

NOTE 16—The following example explains how a balance is selected assume that a test method requires that a sample of soil be graded and that the fractions be reported to the nearest 0 1 % If the sample mass is 1000 g, then a balance having a minimum capability of determining the mass of each fraction to the nearest 1 0 g (0 1 % of the total sample mass) will be required If the sample mass is 5000 g, then a balance having a minimum capability of determining the mass of each fraction to the nearest 5 0 g (0 1 % of the total sample mass) will be required

9 2 *Specifying Balances*—An example of the wording that may be used to specify balances in ASTM standards is as follows

Balance—A balance having a minimum capacity of ____ g or kg and meeting the requirements of Specification D 4753 for a balance of ____ g readability

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard Users of this standard are expressly advised that determination of the validity of any such patent rights and the risk of infringement of such rights are entirely their own responsibility

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised either reapproved or withdrawn Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards 1916 Race St Philadelphia PA 19103

STANDARD OPERATING PROCEDURE

for

Corrective Action

SOP Code ADM - CA

Revision 5

September 12, 2007

PROPRIETARY AND CONFIDENTIAL

Approved by	Quality Assurance	11-12-08 Date
	Chief Quality Officer	11-12-08 Date
	President	11-18-08 Date

© Columbia Analytical Services, Inc , 2007
1317 South 13th Avenue
Kelso, Washington 98626

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials LW Date 11-12-08
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

Standard Operating Procedure for Corrective Action

1 0 PURPOSE

This standard operating procedure (SOP) describes a systematic procedure for documenting nonconforming events and problems (such as errors, deficiencies, deviations, laboratory events, or data that fall outside of established acceptance limits) and the resolution of the nonconformity event or problem (i e , corrective action) A Nonconformity and Corrective Action Report Form is utilized to document (1) identification of the nonconformity and/or problem, (2) investigation of the causes, and (3) corrective actions taken, including, but not necessarily limited to, repetition of the test or analysis Procedures are also described for notifying affected parties, including the CAS customer

The overall purpose of corrective action is to improve the quality of test results to an acceptable level and to maintain the level Corrective action is one part of a comprehensive quality assurance program that emphasizes problem or nonconformity correction (A companion process, preventive action, described in the *SOP for Preventive Action*, emphasizes nonconformity or problem prevention.)

2 0 APPLICABILITY

All CAS employees are to be alert to identifying nonconformities and problems when errors, deficiencies, deviations, or out-of-control situations are detected On-the-spot, remedial corrective actions routinely made by technicians and chemists should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, for example. This SOP establishes a formal system of reporting and documenting corrective actions for (major) nonconformities or problems that affect the quality of the results reported to our customers Examples of nonconformities or problems requiring documentation include, but are not limited to, the following examples

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) containing contaminants above acceptable levels
- Undesirable trends in recoveries of spikes or in relative percent differences between duplicates
- Sample holding time missed
- Unacceptable results in performance evaluation samples
- Deficiencies found during internal or external system audits
- Customer inquiries concerning data quality

CAS PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

CAS

3 0 DEFINITIONS

3 1 Nonconformity

A nonconformity is a departure of a quality characteristic from its intended level or state severe enough to cause an associated product or service not to meet a required specification (American National Standard ANSI/ASQC Z1 4-1981)

3 2 Causes of Nonconformities

PROPRIETARY

The cause of a nonconformity is that agent, situation, or event that produces the nonconformity, error, defect, deviation, problem, or undesirable situation

3 2 1 Chance Causes These are random, unpredictable happenings or events without apparent cause, or the apparent absence of a cause

3 2 2 Assignable Causes (or systematic errors) The causes of a nonconformity due to a known or knowable reason, for example, an error, improper procedure, or an interference in the sample

AND

3 3 Remedial Action

Remedial action is what is done right away to fix the nonconformity or problem and/or what is done short-term until a real fix can be figured out

Remedial action is the tool for fixing the *product* of a process

CONFIDENTIAL

3 4 Corrective Action

Corrective action is the action taken to eliminate the cause(s) of an existing nonconformity, defect, problem, or undesirable situation in order to prevent recurrence (NELAC)

Corrective action is a process that involves (1) root cause analysis, (2) developing a corrective action plan that will prevent recurrence, (3) implementing a corrective action plan that will prevent recurrence, and (4) assessing the action taken to determine its effectiveness

UNCONTROLLED

Corrective action is what is done to fix the *process* so the defect won't happen again

COPY

[1] Denise Robitaille Separating the Shalls from the Shoulds *The Auditor* July August 2007 page 31

3 5 Root Cause Analysis

Root cause analysis is the process of identifying the most basic reason(s) or causal factor(s) for an undesirable condition or problem, which, if eliminated or corrected, would prevent the undesirable condition or problem from existing or recurring

3 6 Error

Errors are a deviation from what is right and correct.

3 7 Blunder

Blunders are errors resulting from carelessness, inattention, misunderstanding, etc

4 0 DISCUSSION

When analytical errors, deficiencies, deviations, out-of-control situations, and undesirable performance are discovered as the result of a laboratory's own quality assessment efforts, from its participation in performance evaluation sample analyses, and from internal and external systems audits, a process is needed for reporting and documenting the correction of these nonconformities or problems and improving performance

The goal of quality assurance is error prevention, not just error correction Accordingly, records are to be kept of nonconformities and problems and the corrective actions that are taken to alleviate them These records are to be regularly reviewed for the effectiveness of the corrective actions as well as for any patterns or persistence of specific nonconformities or problems CAS is committed to continually examining and improving its measurement processes.

5 0 RESPONSIBILITIES

Everyone in the laboratory has the responsibility to perform his or her job according to established specifications and procedures Everyone has the responsibility to know when their work product does not meet the control criteria established for that activity When nonconformities or problems or out-of-control situations occur, everyone has the responsibility to initiate the action of restoring the process to its normal functioning.

Corrective action procedures are often initiated and handled at the bench level by the technician who reviews the data produced by the entire analytical process If the problem persists or cannot be identified by the chemist, the matter is referred to the department supervisor, laboratory manager, or the laboratory's Quality Assurance Program Manager (QA PM) for further investigation

Laboratory management and the laboratory s QA PM are responsible to act upon Nonconformity and Corrective Action Reports (NCARs) Furthermore, laboratory managers are ultimately account able for the follow through, verification, and evaluation of the effectiveness of corrective action(s)

PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

The laboratory s QA PM must review all corrective actions for effectiveness and look for patterns or persistence of specific nonconformities or problems

6 0 PROCEDURE

6 1 Nonconformity Identification

The first objective is to positively identify the kind of nonconformity or problem that is present and whether it is persistent or transitory Determining the cause(s) of a nonconformity can be difficult There are two kinds of causes that affect a measurement process Chance causes occur randomly and affect precision whereas assignable causes can produce bias or unacceptable imprecision Any technically significant nonconformity or problem should be investigated for an assignable cause Assignable causes should be minimized or eliminated, if possible

Table 1 is a checklist that can be used to aid in the identification of nonconformities or problems

6 2 Corrective Action Process

6 2 1 Cause Analysis

The corrective action process begins with an investigation to determine the root cause(s) of the nonconformity or problem

"Cause analysis is the key and sometimes the most difficult part in the corrective action procedure Often the root cause is not obvious and thus a careful analysis of all potential causes of the problem is required Potential causes could include customer requirements, the samples, sample specifications, methods and procedures, staff skills and training, consumables, or equipment and its calibration '[2]

Quality tools such as flowcharts, fishbone diagrams, and why-why diagrams are sometimes useful in determining the root cause of a nonconformity or problem

The cause analysis shall be documented

Table 2 lists examples of common remedial and corrective actions

6 2 2 Corrective Action Plan Development

During the root cause analysis phase (Section 6 2 1), most likely one or more causes will be identified During this phase, one or more plans may be devised

[2] Reference 9 3 Section 4 11 2

COPY PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

that would potentially solve and eliminate the nonconformity or problem One specific plan will be selected and a detailed plan will be developed that will most likely eliminate the nonconformity or problem The goal of the plan is to prevent recurrence The plan may involve, for example, simplifying or redesigning a procedure, retraining personnel, obtaining new materials, obtaining new equipment, or other modifications, or a combination of these things

The corrective action plan development and the selected plan shall be documented

The plan will be communicated to and approved by the affected manager

6 2 3 Corrective Action Plan Implementation

The plan developed in Section 6 2 2 will be implemented The plan will be communicated to the affected personnel To implement the corrective action plan, any necessary changes to the affected process need to be made

The corrective action plan implementation shall be documented

6 2 4 Corrective Action Plan Monitoring

The corrective action that was implemented (in Section 6 2 3) shall be monitored to assess its effectiveness Monitoring may consistent of observation of what was changed, evaluation of data (such as control charts), internal audits, etc

If the corrective action does not eliminate the nonconformity or problem or it is not as effective as desired, it may be necessary to go back (a) to the cause analysis (Section 6 2 1) because the root cause was not identified or (b) to the corrective action plan development (Section 6 2 2) because the plan was flawed for some reason or (c) to the corrective plan implementation (Section 6 2 3) because the plan wasn't being followed, for example

The corrective action plan monitoring shall be documented

6 2 5 Corrective Action Closure

Closure of the corrective action is completed when the implemented corrective action eliminates the nonconformity or problem and the SOP for the process has been revised, approved, and implemented

PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

6 3 Documentation

A Nonconformity and Corrective Action Report (NCAR) is used to (1) document identification and details of the nonconformity, problem, or out-of-control situation, (2) describe the corrective action(s) taken, and (3) provide documentation of approval and customer notification (if necessary) The following instructions are for the NCAR form on page 15 Other NCAR formats may be used as long as the essential components and information are present

6 3 1 Nonconformity

This section of the NCAR is used to document the details of the nonconformity, problem, or out-of control situation

6 3 1 1 NCAR Number This is a number that is assigned to make each NCAR unique and to permit tracking it A suggested format is *yy-nnn*, where *yy* is a two-digit designation for the year and *nnn* is a three-digit counter starting with 001 for the first NCAR of the year

6 3 1 2 Procedure (SOP or Method) Indicate the analysis or activity involved For example, sulfate analysis by Method 300 0

6 3 1 3 Event Date Record the date the nonconformity occurred or was identified

6 3 1 4 Event Check the box next the description of the nonconformity If none of the listed events are appropriate, check the Other box and describe the event

6 3 1 5 Samples/Projects/Customers/Systems Affected List the samples, projects, customers, and/or systems affected by the nonconformity, problem or out-of-control situation If samples are involved, list the lab codes of all the affected samples

6 3 1 6 Detailed Description Describe the nonconformity, problem, or out-of-control situation in detail

6 3 1 7 Originator and Date Fill in the name of the person initiating the NCAR and the date it was prepared

6 3 1 8 Project Manager, Notified by, and Date The Project Manager(s) is(are) to be notified of the nonconformity, problem, or out-of-control situation at this point in the process Fill in the name of the Project Manager(s)

CAS PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

CAS

who was(were) notified, who did the notifying, and the date the Project Manager(s) was(were) notified

6 3 2 Corrective Action and Outcome

This section of the NCAR is used to describe in detail the corrective action and the result Before corrective action is taken, an investigation into the root cause should be done

PROPRIETARY

6 3 2 1 Root Cause Analysis Corrective action should start with an investigation to determine the root cause (Section 6 2) of the nonconformity identified in Section 6 1

6 3 2 2 Corrective Action and Outcome Use this part of the Report to describe in detail what corrective actions were taken to restore the system to acceptable performance Corrective actions need to focus on (1) **fixing** the particular nonconformity (remedial action) and on (2) **preventing** the nonconformity from ever happening again by correcting the root cause (corrective action) The result of the corrective action should also be described (i e , was the corrective action effective and satisfactory?) For example

AND

Nonconformity Sample refrigerator temperature too high, above 6° C
Remedial Action Repairman called in who cleaned the cooling coils
Corrective Action Regular maintenance will include cooling coil cleaning
Outcome Temperature restored to 4° C within 8 hours Thermostat was not adjusted

CONFIDENTIAL

6 3 2 3 Corrective Actions for Out-of-Control Data This subject is addressed in analysis-specific SOPs in a Section with the same title See Reference 9 5

6 3 2 4 Is the data to be flagged in the Analytical Report with an appropriate qualifier? If the sample results are to be reported in spite of the nonconformity, whether or not an appropriate qualifier is to be added onto the results needs to be determined and noted

UNCONTROLLED

6 3 3 Approval and Notification

COPY

This section of the NCAR is used to document verification and approval of the corrective action(s) Customer notification of the nonconformity and corrective action is also documented

6 3 3 1 Supervisor Verification and Approval The supervisor of the person responsible for performing the corrective action(s) verifies, approves, signs, and dates the Report indicating that the corrective action taken is acceptable The supervisor may add comments

6 3 3 2 QA PM Verification and Approval The laboratory's QA PM verifies, approves, signs, and dates the Report indicating that the corrective action taken is acceptable The QA PM may add comments

6 3 3 3 Customer Notification The appropriate box is checked by the Project Manager

6 3 3 4 Project Manager Verification and Approval The Project Manager(s) for the affected samples, projects, and/or customers verifies, approves, signs, and dates the Report indicating that the corrective action taken is acceptable The Project Manager also needs to retain records of pertinent customer communications. The Project Manager may add comments

6 3 4 Filing

6 3 4 1 Samples/Projects/Customers The original NCAR is placed in the project file with the original raw data If more than one service request is involved, the service request or project file containing the original NCAR is noted on the original NCAR and photocopies are placed in the other files A photocopy of the NCAR is returned to the supervisor of the department affected by the nonconformity Another photocopy of the NCAR is given to the QA PM to be filed in a corrective action file

6 3 4 2 Systems The original NCAR is filed with the appropriate system, job, or client file For example, an NCAR for a sample cooler problem would be filed with the daily temperature check logbook or with the sample cooler maintenance file A photocopy of the NCAR is given to the QA PM for filing in a corrective action file

6 4 Audit Findings

Audit findings, from either internal or external audits, are normally written out in some sort of an audit report by the assessor. To document and track corrective actions to the findings from audits, the Audit Finding Response Form on page 16 may be used

QAC PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

6 4 1 Audit Information In this top section of the Form, indicate who is to address the finding, the location where the finding was observed (e g , which department), the date of the audit, a reference of some sort so that the finding and its corrective action can be tracked to completion, and the name of the assessor

6 4 2 Finding Identification by Assessor Indicate the specific QA system or SOP to which the finding pertains For the description of the finding, copy the finding from the assessor's report Either the lab s QA PM or the assessor may make a recommendation of how the finding could be corrected

6 4 3 Corrective Action by Laboratory In this section, either
(a) describe the corrective action that was taken to correct the finding and to prevent its reoccurrence and attach evidence that the corrective action has been implemented, or
(b) describe a plan for correcting the finding with a target completion date

Eventually, a description of the corrective action will be filled in The supervisor affected by the finding needs to verify and approve the corrective action and sign and date

6 4 4 Corrective Action Approval Both the laboratory's QA PM and manager need to verify and approve the corrective action and sign and date

6 5 Unacceptable Performance Testing (PT) Results

An unacceptable PT result is actually a nonconformity and as such it is to be treated as described in this SOP starting with a cause analysis (Section 6 2 1) The following list of checks may be helpful in determining the root cause

- Check for typos or transcription errors, including if the PT vendor used the submitted result
- Check for a calculation error
- Check to make sure the right units were used
- Check if there is an error associated with a dilution, either a wrong dilution was done or a wrong dilution was used in the calculation
- Check batch QC (namely, the method blank, the LCS, the MS, and the duplicate, DLCS, or DMS) if these results were acceptable or if there was some sort of a trend or out of-control result that would have an impact
- Check the analytical sequence (namely, the calibration, CCBs, CCVs, etc) if these results were acceptable or if there was some sort of trend
- Check the analytical sequence for possible carry-over cross contamination
- Check for process or procedure errors

PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

It is important to evaluate if the root cause for an unacceptable PT result is also occurring with the analysis of customers' samples.

The Performance Testing Report Form on page 17 may be used to document the investigation and corrective actions

7 0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

The QA PM is responsible for maintaining a file containing all completed NCARs NCARs should be reviewed periodically by the QA PM for patterns or persistence of specific problems The CAS Chief Quality Officer will review NCAR summary information provided in the Quarterly QA Report to Management prepared by each laboratory's QA PM

8 0 RECORDS

8 1 A record of the identification of the nonconformity (from Section 6 1) needs to be made

8 2 The entire correction action process (from Section 6 2) needs to be documented

8 3 NCARs are to be archived per the instructions in Section 6 3 4

8 4 Completed Audit Finding Response Forms (Section 6 4) are to be archived with the audit report

8 5 A record of the results of the investigation into the cause of unacceptable PT results (Section 6 5) is to be archived with the PT report.

9 0 REFERENCES

9 1 2003 National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems Standard See Appendix A for pertinent text copied from the Standard

9 2 Department of Defense *Quality Systems Manual for Environmental Laboratories*, Final Version 3, January 2006 See Appendix A for pertinent text copied from the *Manual*

9 3 ISO/IEC 17025 2005(E), "General Requirements for the Competence of Testing and Calibration Laboratories." See Appendix B.

9 4 *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1998, Method 1020 B, Quality Control, Section 14

9 5 *SOP for Preparation of SOPs*, SOP Code ADM – SOP, Section 6 3 3 16 Corrective Actions for Out-of-Control Data

CAS PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

CAS PROPRIETARY AND CONFIDENTIAL

10 0 CHANGES FROM PREVIOUS REVISION

- ★ Cover Page and title on Page 2 SOP title changed
- • Section 1 0 First sentence revised, second paragraph revised
- ★ Section 3 3 New term, subsequent Sections renumbered
- • Section 3 4 Second and third paragraphs are new
- • Section 4 0 Revised, former Section 4 1 moved to new Section 6 1, second paragraph is formerly Section 4 2
- • Section 6.0 First paragraph moved to Section 6 3
- • Section 6 1 Formerly Section 4 1
- ★ Section 6 2 New section
- • Section 6 3 Formerly first paragraph in Section 6 0, paragraph revised to include point numbering in first sentence
- • Section 6 3 1 Formerly Section 6 1
- • Section 6 3 1 8 Project Chemist changed to Project Manager
- • Section 6 3 2 Formerly Section 6 2
- • Section 6 3 2 2 In the example, "Corrective Action" changed to "Remedial Action" and "Long-term" changed to "Corrective Action"
- • Section 6 3 3 Formerly Section 6 3
- • Section 6 3 4 Formerly Section 6 5
- ★ Section 6 5 New section
- ★ Section 8 0 All new
- • Reference 9 1 Updated
- • Reference 9 2 Updated
- • Reference 9 3 New
- ★ NCAR Form on Page 15 Updated
- ★ Performance Testing Report Form on Page 17 New
- • Appendix A New
- • Appendix B New

UNCONTROLLED COPY

CAS

TABLE 1

Deficiency Correction Checklist

Possible Problem		A	B
Procedural Change		*	*
Sampling		*	
Sample Handling		*	*
Analytical Procedure:	Calculations	*	*
	Data	*	*
	Reagents		*
	Equipment		*
	Calibration		*
	Maintenance		*
	Methodology	*	*
Blunder		*	*

PROPRIETARY AND CONFIDENTIAL

A = The measurement process is in control, but the results are questioned or are questionable

B = The measurement process is out-of-control

UNCONTROLLED COPY

CAS

TABLE 2

Examples of Common Remedial and Corrective Actions

QC Activity	Example Acceptance Criteria	Example Remedial and Corrective Actions
Initial Instrument Blank	Instrument response < MDL	Prepare another blank If same response, determine cause of contamination reagents, environment, instrument or equipment failure, etc.
Initial Calibration Standards	Correlation coefficient ≥0 995, %RSD < 20	Reanalyze standards If still unacceptable remake standards and reanalyze
Initial Calibration Verification Standard (ICV)	± 15% of expected value	Reanalyze ICV If still unacceptable, remake and reanalyze initial calibration standards If still unacceptable, use new primary standards to make new calibration standards and recalibrate
Continuing Calibration Verification Standards (CCV)	± 15% of expected value	Reanalyze standard If still unacceptable, recalibrate and reanalyze samples from last acceptable CCV
Method Blank	< MDL or <MRL	Reanalyze the method blank If still unacceptable, determine source of contamination If necessary, reprocess the batch of samples
Laboratory Control Sample (LCS)	±10% of expected value	Reanalyze LCS If still unacceptable, reprocess the batch of samples

PROPRIETARY AND CONFIDENTIAL
UNCONTROLLED COPY

CAS

Nonconformity and Corrective Action Report

NONCONFORMITY

NCAR No ____

PROCEDURE (SOP or METHOD) EVENT DATE ____

EVENT
- ☐ Missed Holding Time
- ☐ Method Blank Contamination
- ☐ Equipment Failure
- ☐ SOP Deviation
- ☐ QC Failure
- ☐ Login Error
- ☐ Unacceptable PT Sample Result
- ☐ Other (describe):
- ☐ Lab Error (spilled sample, spiking error etc.)
- ☐ Project Management Error

SAMPLES / PROJECTS / CUSTOMERS / SYSTEMS AFFECTED

PROPRIETARY

DETAILED DESCRIPTION

ORIGINATOR ____ DATE ____

PROJECT MANAGER(S): ____ NOTIFIED BY: ____ DATE: ____

AND

CORRECTIVE ACTION AND OUTCOME

Re-establishment of conformity must be demonstrated and documented. Describe the steps that were taken, or are planned to be taken, to correct the particular Nonconformity and prevent its reoccurrence, include Project Manager instructions here.

Is the data to be flagged in the Analytical Report with an appropriate qualifier? ☐ No ☐ Yes

CONFIDENTIAL

APPROVAL AND NOTIFICATION

Supervisor Verification and Approval of Corrective Action ____ Date: ____
Comments,

QA PM Verification and Approval of Corrective Action ____ Date ____
Comments

Customer Notified by: ☐ Telephone ☐ Fax ☐ Email ☐ Narrative ☐ Not notified

Project Manager Verification and Approval of Corrective Action ____ Date ____
Comments

(Attach record or cite reference where record is located.)

UNCONTROLLED COPY

AUDIT FINDING RESPONSE FORM

To _____ Location: _____ Audit Date _____

Finding Reference _____ Assessor _____

FINDING IDENTIFICATION BY ASSESSOR

QA System or SOP Affected _____

Description of Finding _____

The following action is recommended to correct this finding and prevent recurrence _____

CORRECTIVE ACTION BY LABORATORY

Describe the corrective action that was taken to correct this finding and to prevent recurrence and attach evidence that the corrective action has been implemented
<<Alternatively, describe a plan for correcting the finding with a target completion date >>

Proposed By: _____ Date: _____

Supervisor Verification and Approval of Corrective Action _____ Date: _____

CORRECTIVE ACTION APPROVAL

The corrective action taken is Acceptable / Not Acceptable

QA PM Verification and Approval of Corrective Action _____ Date _____

Lab Mgr Verification and Approval of Corrective Action _____ Date _____

PROPRIETARY AND CONFIDENTIAL
UNCONTROLLED COPY

CAS

Performance Testing Report
PT Study [fill in study number]

Laboratory's Response to "Not Acceptable" Result

PT Sample	
Method Description	
Analytes	
Reported Values	
Assigned Value	
Acceptance Limits	
NCAR Reference	

Response (Description of laboratory's investigation and corrective actions)

PROPRIETARY AND CONFIDENTIAL

Quality Assurance Program Manager Date

UNCONTROLLED COPY

CAS

Appendix A
Pertinent Text Copied from
2003 NELAC Standard (Reference 9 1) and the DoD Quality Systems Manual (Reference 9 2)

Control of Nonconforming Environmental Testing Work (NELAC Section 5 4 9, DoD Section 4 9)

1 [illegible]

PROPRIETARY

AND

2 [illegible]
NELAC [illegible] DoD [illegible]

Corrective Action (NELAC Section 5 4 10, DoD Section 4 10)

1 General

CONFIDENTIAL

2 Cause Analysis

[illegible]

3 Selection and Implementation of Corrective Actions

UNCONTROLLED

[illegible]

COPY

4 Monitoring of Corrective Actions

[illegible]

5 Additional Audits

CAS PROPRIETARY AND CONFIDENTIAL UNCONTROLLED COPY

6 Technical Corrective Action

SOPs

DoD QSM Clarification Box 19
Audits – Corrective Action

Monitoring of Corrective Actions

Regular Review

- O
- D
- D

Reference

CAS

Appendix B
Pertinent Text Copied from
ISO/IEC 17025:2005(E) Standard (Reference 9 3)

4 11 Corrective action

4 11 1 General

PROPRIETARY

NOTE A

4 11 2 Cause analysis

AND

NOTE C

4 11 3 Selection and implementation of corrective actions

CONFIDENTIAL

4 11 4 Monitoring of corrective actions

4 11 5 Additional audits

UNCONTROLLED
COPY

NOTE S

STANDARD OPERATING PROCEDURE

PCBS AS AROCLORS
SOC-8082Ar
Revision 13
June 25, 2009

UNCONTROLLED

Approved By _____ Supervisor — Date 6/29/09

_____ QA Manager — Date 6/29/09

_____ Laboratory Manager — Date 6/29/09

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2009

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

PCBS AS AROCLORS

1 SCOPE AND APPLICATION

This procedure is used to determine the concentrations of PCBs as Aroclors using EPA Method 8082 This procedure is typically applied to water sediment and soil matrices but may also be applicable to tissue or various miscellaneous waste samples Table 1 lists the analytes that are determined by this procedure and lists the method reporting limits (MRLs) for each compound in water and soil Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL) and Practical Quantitation Limit (PQL) Therefore, MRL=EQL=PQL The reported MRL may be adjusted if required for specific project requirements however, the capability of achieving other reported MRLs must be demonstrated. Method Detection Limits that have been achieved are given in Attachment A MDLs may change as repeat studies are conducted

UNCONTROLLED COPY

2 METHOD SUMMARY

2 1 This procedure provides gas chromatographic conditions for the detection of parts per-billion (ppb) levels of PCBs The target PCBs are extracted from samples using the appropriate procedure for the sample matrix (see applicable SOP) analyzed, and reported as Aroclors Liquid samples are extracted using continuous liquid-liquid extraction (Method 3520 CAS SOP EXT-3520) or when allowed, using solid phase extraction (Method 3535 CAS SOP EXT-3535) Soil/sediment samples are extracted using Soxhlet (Method 3540, CAS SOP EXT-3540) or automated Soxhlet extraction (Method 3541 CAS SOP EXT-3541) An aliquot of the extract is injected into the gas chromatograph (GC) The compounds are separated on a fused silica capillary column Compounds of interest are detected by an electron capture detector Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard and by comparison of elution patterns to those of Aroclor standards Quantitative analysis is performed by using the authentic standard to produce a calibration factor or calibration curve and using the calibration data to determine the concentration of an analyte in the extract The concentration in the sample is calculated using the sample weight or volume and the extract volume

2 2 The sensitivity of this method usually depends on the level of interferences rather than on instrument limitations If interferences prevent detection of the analytes GPC florisil column cleanup sulfur cleanup, or concentrated sulfuric acid cleanups are used to eliminate interferences in the analysis Refer to section 4 2 for cleanup procedure references

3 DEFINITIONS

Analysis Sequence Samples are analyzed in a set referred to as an analysis sequence The sequence begins with instrument calibration followed by sample extracts interspersed with calibration standards The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded

Initial (or Independent) Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration Once it is determined there is no systematic error in preparation of the calibration standards, they are considered valid for subsequent calibrations (as methods and expiration dates allow) The ICV standards are prepared from a materials obtained from a source different from that used to prepare calibration standards

UNCONTROLLED COPY

Matrix Spike/Duplicate Matrix Spike Analysis - In the matrix spike analysis, predetermined quantities of stock solutions of selected Aroclors are added to a sample matrix prior to sample extraction and analysis The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses Samples are split into duplicates, spiked, and analyzed Percent recoveries are calculated for each of the analytes detected The relative percent difference between the samples is calculated and used to assess analytical precision The concentration of the spike should be at 5 to 10 times the MRL or at levels specified by a project analysis plan

Standard Curve - A standard curve is a calibration curve which plots concentrations of a known analyte standard versus the instrument response to the analyte

Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples The purpose of the surrogates is to evaluate the preparation and analysis of samples These compounds are spiked into all blanks, standards, samples, and spiked samples prior to analysis Percent recoveries are calculated for each surrogate

Method Blank - The method blank is an artificial sample designed to monitor introduction of artifacts into the process The method blank is carried through the entire analytical procedure

Continuing Calibration Verification Standard (CCV) A standard injected into the instrument at specified intervals and is used to verify the initial calibration

Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each GC column and instrument used for sample analysis The purpose of the instrument blank is to determine the levels of contamination associated with the

3 DEFINITIONS

Analysis Sequence - Samples are analyzed in a set referred to as an analysis sequence The sequence begins with instrument calibration followed by sample extracts interspersed with calibration standards The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded

Initial (or Independent) Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration Once it is determined there is no systematic error in preparation of the calibration standards, they are considered valid for subsequent calibrations (as methods and expiration dates allow) The ICV standards are prepared from a materials obtained from a source different from that used to prepare calibration standards.

UNCONTROLLED

Matrix Spike/Duplicate Matrix Spike Analysis - In the matrix spike analysis, predetermined quantities of stock solutions of selected Aroclors are added to a sample matrix prior to sample extraction and analysis The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses Samples are split into duplicates, spiked, and analyzed Percent recoveries are calculated for each of the analytes detected The relative percent difference between the samples is calculated and used to assess analytical precision The concentration of the spike should be at 5 to 10 times the MRL or at levels specified by a project analysis plan

COPY

Standard Curve - A standard curve is a calibration curve which plots concentrations of a known analyte standard versus the instrument response to the analyte

Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples The purpose of the surrogates is to evaluate the preparation and analysis of samples These compounds are spiked into all blanks, standards, samples, and spiked samples prior to analysis Percent recoveries are calculated for each surrogate

Method Blank - The method blank is an artificial sample designed to monitor introduction of artifacts into the process The method blank is carried through the entire analytical procedure

Continuing Calibration Verification Standard (CCV) - A standard injected into the instrument at specified intervals and is used to verify the initial calibration

Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each GC column and instrument used for sample analysis The purpose of the instrument blank is to determine the levels of contamination associated with the

instrumental analysis itself particularly with regard to the carry over of analytes from standards or highly contaminated samples into other analyses

4 INTERFERENCES

4 1 Interferences by phthalate esters can pose a major problem in PCB determinations when using the electron capture detector These compounds generally appear in the chromatogram as large late-eluting peaks especially in the 15% and 50% fractions from the florisil cleanup Common flexible plastics contain varying amounts of phthalates These phthalates are easily extracted or leached from such materials during laboratory operations Phthalate contamination is not usually a problem in our laboratory operation

UNCONTROLLED

4 2 Co-extractables such as lipids, waxes, etc , can be removed via GPC cleanup (CAS SOP SOC-3640A). Certain fractionization cleanups can be used to selectively remove organochlorine pesticides, aiding in Aroclor determination (CAS SOP SOC-3665) The presence of elemental sulfur will result in interferences for most Aroclors If GPC cleanup is insufficient cleanup via Method 3660 (CAS SOP SOC-3660) may be used for the removal of sulfur

5 SAFETY

5 1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however each chemical compound should be treated as a potential health hazard Exposure to these compounds should be reduced to the lowest possible level

COPY

5 2 Follow all applicable safety procedures as described in the CAS Safety Manual A reference file of material safety data sheets is available to all personnel involved in these analyses CAS also maintains a file of OSHA regulations regarding the safe handling of the chemicals specified in this method

6 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6 1 Containers used to collect samples should be purchased pre-cleaned containers Alternatively, containers may be soap and water washed followed by methanol (or isopropanol) rinsing The sample containers should be of glass or teflon and have screw-top covers with teflon liners In situations where teflon is not available solvent-rinsed aluminum foil may be used as a liner Highly acidic or basic samples may react with the aluminum foil causing eventual contamination of the sample Plastic containers or lids may <u>not</u> be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic

6 2 Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves thus causing contamination Samples

should not be collected or stored in the presence of exhaust fumes If the sample comes in contact with the sampler (e g if an automatic sampler is used), run reagent water through the sampler and use the rinseate as a field blank

6 3 Samples should be tested for residual chlorine at the time of sampling For aqueous samples with residual chlorine present add 3-mL 10% sodium thiosulfate solution per gallon (0 008%)

6 4 Water and soil samples must be iced or refrigerated at 4 ± 2°C from time of collection until extraction Tissue samples should be stored in accordance with project requirements, typically refrigerated or frozen

UNCONTROLLED

6 5 Water samples must be extracted within 7 days and the extracts analyzed within 40 days Soil samples must be extracted within 14 days and the extract analyzed within 40 days Extracts are stored under refrigeration until analysis

7 APPARATUS AND EQUIPMENT

7 1 Gas Chromatograph (GC)

7 1 1 Analytical system complete with gas chromatograph suitable for splitless or on-column automated injection into a wide bore capillary column with an electron capture detector (ECD) Use of Large Volume Injection (LVI) is optional Helium is used as the carrier gas; argon/methane mixture is used for the detector makeup gas (auxiliary gas) Current instrumental systems are identified as follows

COPY

Instrument I D	Analytical System	Routine Matrix
GC09	H-P 5890	Water/Soil/Tissue
GC22	Agilent 6890	Water-LL/Tissue
GC32	Agilent 6890	Water/Soil/Tissue

7 1 2 GC Autosampler The GC system should be configured with a compatible autosampler for automated injection of standards, samples, and QC samples

7 1 3 GC Columns - fused silica capillary columns
Column 1 DB-35MS 30-m x 0 53mm, 1 0um film thickness, or equivalent
Column 2 DB-XLB 30-m x 0 53mm, 1 5um film thickness, or equivalent

Note Column diameter and film thickness varies depending on the column Refer to the instrument maintenance logbook for the column used for a specific instrument configuration

7 1 4 Data System - A computer data system must be interfaced to the GC/ECD The system allows the continuous acquisition and storage on machine-readable media of chromatographic data obtained throughout the duration of the analysis program

The computer must have software that includes automated calibration identification, and quantitation routines The software must also be capable of integrating the chromatographic peaks abundances The current version of the manufacturer s software is preferred (Target or HP Chemstation/Enviroquant)

8 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

8 1 Solvents Hexane, acetone, methylene chloride, isooctane, and methanol Pesticide grade or equivalent

8 2 Standards

UNCONTROLLED

8.2.1 The following commercially prepared stock standards and ICV stock standards are purchased from various reputable vendors and must be certified by the manufacturer The ICV stock standards are obtained from a different source from the initial calibration Transfer stock standard solutions into Teflon-sealed screw-cap bottles Stock standard solutions are stored at -10° C, or at ambient temperature as recommended by the vendor and protected from light The expiration date for unopened ampules is the manufacturer's assigned expiration date If the manufacturer does not assign a date, an expiration date of 1 year from receipt is assigned Check stock standards frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them

COPY

Standard	Concentration	Use
8081/8082 Surrogate	200 ug/mL	ICAL
Aroclor 1016	1000 ug/mL	ICAL
Aroclor 1221	1000 ug/mL	ICAL
Aroclor 1232	1000 ug/mL	ICAL
Aroclor 1242	1000 ug/mL	ICAL
Aroclor 1248	1000 ug/mL	ICAL
Aroclor 1254	1000 ug/mL	ICAL
Aroclor 1260	1000 ug/mL	ICAL
Aroclor 1262	1000 ug/mL	ICAL
Aroclor 1268	1000 ug/mL	ICAL
Aroclor 1016	100 ug/mL	ICV
Aroclor 1221	100 ug/mL	ICV
Aroclor 1232	100 ug/mL	ICV
Aroclor 1242	100 ug/mL	ICV
Aroclor 1248	100 ug/mL	ICV
Aroclor 1254	100 ug/mL	ICV
Aroclor 1260	100 ug/mL	ICV
Aroclor 1262	100 ug/mL	ICV
Aroclor 1268	100 ug/mL	ICV

8 2 2 Intermediate Aroclor calibration standard solutions are made by diluting 1000 ug/mL stock standards 1 20 in hexane An intermediate surrogate standard is prepared at 5ug/mL by diluting the stock 1 40 in hexane No ICV intermediates are prepared

8 2 3 Prepare calibration standards at a minimum of five concentration levels containing equal concentrations of both Aroclors 1016 and 1260 by dilution of the intermediate standards with hexane One of the concentration levels should be at or below a concentration representing the method reporting limit (MRL) The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC See Table 3 for preparation and concentrations, including standards designated as CCVs A calibration standard of mid-range concentration is used for the CCV

UNCONTROLLED

8 2 4 The independent calibration verification (ICV) standards are prepared from stock solutions from a different source from the initial calibration as listed in Table 3 Expiration periods are the same as for equivalent stock and calibration standards

8 2 5 Standards of the other Aroclors are prepared for use as retention time/pattern standards and to establish calibration factors for these Aroclors (see Table 3)

COPY

8 2 6 Calibration standard solutions are stored at 4 ± 2°C, or at ambient temperature as recommended by the vendor, and must be replaced after six months, or sooner, if comparison with check standards indicate a problem

8 2 7 A surrogate spiking solution is prepared at 2 ug/mL by making a 1 100 dilution of the surrogate stock standard in acetone The surrogate solution is stored in the refrigerator for up to six months

8 2 8 Matrix spike solution Prepare a spiking solution at 40 ug/mL containing both Aroclor 1016 and 1260 by diluting the 1000 ug/mL stock standards 1 25 with acetone

9 PREVENTIVE MAINTENANCE

9 1 All maintenance activities are recorded in a maintenance logbook kept for each instrument

9 2 Carrier gas - Inline purifiers or scubbers should be in place for all sources of carrier gas These are selected to remove water, oxygen and hydrocarbons Purifiers should be changed as recommended by the supplier

9 3 Gas Chromatograph

9 3 1 Whenever GC maintenance is performed care should be taken to minimize the introduction of air or oxygen into the column Injection port maintenance includes changing the injection port liner seal, washer o-ring, septum column ferrule and autosampler syringe as needed Liners and seals should be changed when recent sample analyses predict a problem with chomatographic performance In some cases liners and seals may be cleaned and re-used

9 3 2 Clipping off a small portion of the head of the column often improves chromatographic performance When cutting off any portion of the column, make sure the cut is straight and "clean" (uniform, without fragmentation) by using the proper column cutting tool

UNCONTROLLED

9 3 3 Over time, the column will exhibit poorer overall performance as contaminated sample matrices are analyzed The length of time for this to occur will depend on the samples analyzed When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement the column should be replaced This is especially true when evident in conjunction with calibration difficulties

10 RESPONSIBILITIES

COPY

10 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

10 2 It is the responsibility of the department supervisor/manager to document analyst training Documenting method proficiency as described in 8082, is also the responsibility of the department supervisor/manager

11 PROCEDURE

11 1 Sample Preparation

11 1 1 Water samples (1L) are extracted at a pH of 5-9 with methylene chloride, using Method 3520 (CAS SOP EXT-3520) or when allowed, using solid phase extraction (CAS SOP EXT-3535) Refer to the applicable extraction SOP For extraction by 3535 acidification of the sample prior to extraction may be allowable if project objectives and performance requirements of methods 3535 and 8081 are met An ultra low-level water option may be used, where a 1L sample

amount and a final extract volume of 2mL is used Large Volume Injectors are typically used with this option

Note Project-specific or regulation-specific extraction methods may apply For projects originating from South Carolina and under the SC DHEC lab certification use the 3520 extraction method only

11 1 2 Soil/sediment samples are extracted using either EPA Method 3540 (CAS SOP EXT-3540) or method 3541 (CAS SOP EXT-3541) Refer to the applicable extraction SOP A low-level sediment option may be used where the sample weight of 40g (20g dry weight) and a final extract volume of 4mL is used

11 1 3 Additional sample cleanup procedures may be employed as appropriate for the samples. Refer to the section on interferences and the appropriate CAS SOP

UNCONTROLLED

11 2 Calibration

11 2 1 The default calibration procedures are given in the following sections and, at the time of this revision follow Method 8000B The analyst should also refer to the CAS SOP for Calibration of Instruments for Organics Chromatographic Analyses (SOC-CAL), where calibration procedures and policies are described The calibration procedure(s) and options chosen must follow the CAS protocols

Note Certain state or program protocols have specific procedures for calibration This may include all or part of Method 8000C The analyst must ensure that the correct procedures are used Known exceptions to 8000B are as follows

COPY

- Arizona DHS requires the use of Method 8000C calibration procedures for projects originating in Arizona and under the AZ DHS lab licensure Refer to the AZDHS calibration guidance document at the following online location http //www azdhs gov/lab/license/tech/8000cmethod pdf

Note The use of 'averaging' of %RSDs or CCV %D (a k a grand mean) is not allowed for projects under the DoD QSM protocols

Note The use of quadratic regression calibration is not allowed for projects (samples) originating from South Carolina and under the SC DHEC lab certification

11 2 2 Prepare a minimum of 5 calibration standards containing equal concentrations of both Aroclor 1016 and 1260 by dilution of the stock standard(s) with isooctane or hexane Single standards of each of the other target Aroclors are required to aid the analyst in pattern recognition Once the linearity of the detector has been demonstrated using Aroclor 1016/1260 standards the single standards of the remaining target Aroclors are also used to determine the calibration factor for each

Aroclor Prepare a standard for each of the other Aroclors The concentrations should correspond to the mid-point of the linear range of the detector

A minimum of 3 peaks must be chosen for each Aroclor, and preferably 6 peaks The peaks must be characteristic of the Aroclor in question Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak For each Aroclor, the set of 3 to 6 peaks should include at least one peak that is unique to that Aroclor Use at least five peaks for the Aroclor 1016/1260 mixture none of which should be found in both of these Aroclors Establish the retention time window position using the mid point of the ICAL range before processing the calibration curve

UNCONTROLLED

11 2.3 Calibrate the system immediately prior to conducting any analyses. Refer to Table 2 for instrument conditions Starting with the standard of lowest concentration, analyze each 1016/1260 calibration standard and tabulate response (peak area) versus the concentration in the standard Refer to Table 2 for instrument conditions Calculate the ratio of the response to the amount injected the (calibration factor) for each analyte at each standard concentration For 1016/1260 and DCB the Relative Standard Deviation (RSD) must be less than 20% when average response factor is used

11 2 4 Analyze each of the single-point calibration standards of the other target Aroclors Calculate the calibration factor (CF) for each analyte at each standard concentration

COPY

11 2 5 Each calibration of each Aroclor is verified by an independent source Prepare an independent calibration verification standard (ICV) by dilution of a stock solution purchased from a different vendor and analyze immediately after each initial calibration Calculate the concentration using the typical procedure used for quantitation Calculate the percent difference (%D) from the ICV true value Evaluate the ICV as described in the SOP for Calibration of Instruments for Organics Chromatographic Analyses

Note DoD ICV acceptance criteria is ± 20% from the analytes assigned value

11 3 Calibration Verification

11 3 1 The working calibration curve or calibration factor must be verified on each analytical sequence by the analysis of one or more mid range calibration standards (CCV) A standard (CCV) must be injected at the start of each sequence and after each set of sample extracts (every 10 samples or every 12 hours, whichever is first) in the analysis sequence

Note DoD projects require a CCV analysis every 10 field samples

11 3 2 The acceptance criterion for all analytes in the CCV analysis is a response (RF or concentration) within ±15% D of the expected value, as compared to the initial calibration Refer to the CAS protocols for organics analyses calibration for CCV evaluation protocols

Note DoD CCV acceptance criteria is ± 20% from the analytes assigned value

11 4 Retention Time Windows

11 4 1 Pattern recognition/matching and retention times are used for the identification of PCBs as Aroclors

UNCONTROLLED

11 4 2 Establish retention time windows for the peaks used for quantitation with the GC system in acceptable operating condition Make three injections of all analytes throughout the course of a 72-hour period Serial injections over less than a 72-hour period may result in retention time windows that are too tight Using retention times from these analyses, calculate retention time windows Refer to EPA Method 8000B for detailed instructions

11 4 3 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window, however the experience of the analyst should weigh heavily in the interpretation of chromatograms. In those cases where the standard deviation for a particular standard is zero, the laboratory may use a default window of ± 0 03 minutes If the peak width is > 0.06 minutes, use a default window of 0 1 minutes

COPY

11 4 4 Calculate retention time windows for each standard on each GC column and whenever a new GC column is installed Retain this data in the method file

11 5 Gas Chromatography

11 5 1 Set up an analytical sequence for the standards and samples to be analyzed Calibrate the system as described in Section 11 2 Refer to Table 2 for typical instrument operating conditions The same conditions must be used for samples as for calibration and QC analyses Ensure that the instrument configuration is correct and that any necessary maintenance has been performed Figure 1 shows a typical analysis sequence

Note For DoD projects, the CCB must be analyzed following the CCV Instrument blanks/CCBs may not be analyzed prior to QC samples or standards

11 5 2 Evaluate the CCVs as indicated in Section 11 3 Use the standards interspersed throughout the sample analysis sequence to evaluate the qualitative performance of the GC system including positioning of the retention time window If any retention time shift which would impede analyte identification is evident (as shown by Aroclor pattern irregularities or the surrogate falling outside of the retention

time window), evaluate the chromatogram for possible causes such as carryover from a highly contaminated sample If a problem related to GC system has been determined to be the cause of retention time shift perform whatever maintenance is necessary before reanalyzing the CCV or recalibrating and proceeding with sample analysis All samples that were injected after the sample exceeded the criteria must be reinjected if initial analysis indicated the presence of any analytes of interest

FIGURE 1

Analysis Sequence

UNCONTROLLED COPY

Initial Calibration Blank	ICB
Standard 1	1221 midpoint
Standard 2	1232 midpoint
Standard 3	1242 midpoint
Standard 4	1248 midpoint
Standard 5	1254 midpoint
Standard 6	1262 midpoint
Standard 7	1268 midpoint
Standards 8-12	1016/1260 ICAL standards
Standards 13-20	ICVs for 1016 1221, 1232 1242 1254 1260 1262 1268
Continuing Calibration Blank	CCB
Continuing Calibration Verification	CCV
Method Blank	
Laboratory Control Sample	LCS
Sample 1	
Sample 2	
Sample 3	
Sample 4	
Sample 5	
Sample 6	
Sample 7	
Sample 8	
Matrix Spike	
Duplicate Matrix Spike	
Continuing Calibration Blank	CCB
Continuing Calibration Verification	CCV
Sample 9	
Sample 10	
etc	
etc	

Continuing Calibration Blank	CCB
Continuing Calibration Verification	CCV

Note If a valid 1016/1260 initial calibration is in place, a new set of initial calibration standards may not be required In this case, CCV standards are analyzed at the beginning of the sequences in place of initial calibration standards

Note For DoD projects the CCB must be analyzed following the CCV Instrument blanks and CCBs may not be analyzed prior to QC samples or standards

11 6 Troubleshooting

UNCONTROLLED

11 6.1 Initial calibration – If the initial calibration fails to meet the criteria, or the ICV fails (indicating a calibration problem), the following steps may be taken, depending on nature of the problem

- Recheck the information entered into the software used for calibration and quantitation Verify the standard values are correct and datafiles are correct If incorrect repeat the calibration with the correct information
- Recheck standards preparation to ensure that standards are correct Re-prepare and reanalyze if needed
- Ensure that proper preventive maintenance was performed Repeat the preventive maintenance if necessary and reanalyze the calibration
- If calibration problems persist or more substantial calibration problems exist corrective maintenance or repair may be needed This includes such measures as column changes, detector maintenance or GC repair This will depend on the nature of the problem Following any such maintenance, repeat the calibration

COPY

11 6 2 Continuing calibration – If the CCV analysis fails to meet the criteria, the following steps may be taken, depending on nature of the problem

- Recheck the information entered into the software used for calibration and quantitation Verify the standard values are correct and datafiles are correct If incorrect, repeat the calibration with the correct information
- Recheck standards preparation to ensure that standards are correct and that the correct standard is used as the CCV Re-prepare and reanalyze if needed Note that NELAC and DoD requirements apply when multiple CCVs are analyzed
- Ensure that proper preventive maintenance was performed Repeat the preventive maintenance if necessary and reanalyze the CCV
- If calibration problems persist or more substantial calibration problems exist, corrective maintenance or repair may be needed This includes such measures as column changes detector maintenance or GC repair This

will depend on the nature of the problem Following any such maintenance repeat analysis of the CCV and necessary samples Major maintenance will require recalibration Note that some samples may quickly deteriorate the system to the point that closing CCVs will not pass This should be verified through a second run of the samples and documented

12 QA/QC REQUIREMENTS

12 1 Refer to Section 8 0 of Method 8082 for general QC protocol In addition to instrument criteria for calibration, the ability of each analyst/instrument to generate acceptable accuracy and precision must be documented prior to sample analysis (IPR study) This must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made To do this, four reagent water samples are spiked with each target analyte, extracted, and analyzed Refer to Method 8082 for this requirement and acceptance criteria

UNCONTROLLED

12 2 Method Detection Limits

12 2 1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure Spike a minimum of seven blank replicates with a MDL spiking solution (at a level below the MRL) for each target analyte, extract, and analyze The MDL studies should be done for each matrix prep method, and instrument Refer to the CAS *SOP for The Determination of Method Detection Limits*

12 2 2 Calculate the average concentration found (x) in the sample concentration, and the standard deviation of the concentrations for each analyte Calculate the MDL for each analyte using the correct T value for the number of replicates The MDL study should be done annually

12 3 Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the *SOP for Sample Batches* The Quality Assurance Manual (Section 12) provides guidance for interpretation of QC results Ongoing QC samples include

12 3 1 Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences The method blank must demonstrate that interferences from the analytical and preparation steps minimized No target analytes should be detected above the MRL in the method blank

Note DoD projects require no analytes detected > ½ the RL or > 1/10 the regulatory limit

12 3 2 A lab control sample (LCS) must be extracted and analyzed with every batch of 20 samples The water LCS is prepared by adding 50 µL of the matrix spike solution to 1L of reagent water resulting in a concentration of 2 0 ug/L The soil LCS is prepared by adding 100 µL of spike solution to 20g of sand, resulting in a concentration of 200 ug/kg For project specific low-level extractions spiking amounts can be adjusted accordingly Calculate percent recovery (%R) as follows

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

UNCONTROLLED

Acceptance criteria for lab control samples are listed in Attachment A Project-specific or program-specific acceptance criteria may supersede CAS criteria For example, for samples requiring South Carolina DHEC certification the acceptance criteria are 70-130 % recovery If the lab control sample (LCS) fails acceptance limits for any of the compounds, the analyst must evaluate the system and calibration If no problems are found, corrective action must be taken The acceptance criteria listed are current criteria, but are subject to change as control limits are updated

COPY

12 3 3 A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples The MS/DMS is prepared by adding the same volume of the matrix spike solution to the sample as listed for the LCS then proceeding with the entire extraction and analysis Calculate percent recovery (%R) as follows

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as

$$RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where R1 = % recovery of the MS
R2 = % recovery of the DMS

Acceptance criteria for matrix spikes are listed in Attachment A If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects corrective action must be taken The acceptance criteria listed are current criteria but are subject to change as control limits are updated

12 3 4 Surrogate spike is added to every sample blank and spike prior to extraction Two surrogate standards (tetrachloro-m-xylene and decachlorobiphenyl) are added to each sample For water, 100μL of the surrogate spike is added to 1L, resulting in 0 2 ug/L For soil, 200μL of the surrogate spike is added to 20g, resulting in 20 ug/kg Calculate surrogate percent recovery (%R) as

UNCONTROLLED

$$\%R = S/V \times 100$$

Where S = The amount of surrogate recovered
V = The amount spiked/final volume

The acceptance limits for the surrogates are given in Attachment A Both surrogate recoveries must be within the acceptance limits If either (or both) surrogate is outside of acceptance limits for reasons other than matrix interferences corrective action must be taken Corrective actions include recalculation, reanalysis, or reextraction and reanalysis The acceptance criteria listed are current criteria, but are subject to change as control limits are updated

COPY

12 3 5 Additional QA/QC measures include control charting of QC sample results

12 4 Troubleshooting

12 4 1 Method blanks - If the method blank fails to meet the criteria, the sample data in the associated batch should be examined If all samples and QC have hits for the analyte samples and QC should be re-extracted and reanalyzed as necessary (samples with higher level hits may not need reanalysis) It should be verified through the analysis of instrument blanks that the problem is isolated to either the GC of the sample preparation If the problem is isolated to the MB the data may be flagged and narrated Also refer to Section 12 of the QA Manual for flowcharts

The source of MB contamination should be isolated and corrected as soon as possible to prevent further failures

12 4 2 Surrogate, LCS and MS QC Data - Refer to Section 12 of the QA Manual for flowcharts addressing data interpretation and corrective actions

13 DATA REDUCTION, REVIEW, AND REPORTING

13 1 Identification of PCBs as Aroclors

13 1 1 To identify Aroclors, compare the chromatographic pattern of the sample to known Aroclor standards Tentative identification of PCBs as Aroclors is made when the pattern of peaks in the sample chromatogram matches the pattern of peaks in the Aroclor standard itself There also needs to be agreement between the retention times and response ratios of the 3-6 selected quantitation peaks in the sample chromatogram and the Aroclor standard

UNCONTROLLED

13 1 2 Tentative identification of analytes must be confirmed using a second GC column of dissimilar phase Identify the Aroclor by comparing the chromatographic pattern of the sample to known Aroclor standards analyzed on the same column Confirmation of the Aroclor is made when the sample chromatogram matches the pattern of peaks in the Aroclor being confirmed Quantitations for the 2 columns must agree ($\leq$ 40%RPD) to confirm the identification If interferences or other sample anomalies make the RPD value >40% but the analyst makes a positive identification, the basis of the identification must be documented and the data user notified of the discrepancy (see section 13 2)

COPY

13 2 Sample matrix difficulties

13 2 1 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the pattern of a specific Aroclor so it does not closely match an Aroclor standard The earlier eluting peaks will often diminish in comparison to the later eluting peaks If this is observed, alternate peaks may be selected to aid identification to reduce quantitation bias

13 2 2 Metabolism by organisms may also alter the pattern since individual PCB congeners are metabolized at different rates When working with tissue samples the 40% RPD criteria for confirmation may not be met

13 2 3 Samples may also include mixtures of two or more Aroclors To the extent possible identify and quantify each Aroclor

13 2 4 High amounts of organochlorine pesticides in the sample may interfere with identification If this is observed, alternate peaks may be selected to aid identification to reduce quantitation bias Certain fractionization cleanups can be used to selectively remove organochlorine pesticides, aiding in Aroclor determination (Acid cleanup, CAS SOP SOC-3665)

13 2 5 For all of these reasons a high level of analyst expertise is required to interpret complex chromatograms

13 3 Quantitation of PCBs as Aroclors

13 3 1 The quantitation of PCBs as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard or standards All calibration acceptance criteria as described in section 11must be met before reporting any results Sample results should then be reported according to the organics confirmation Sop (SOC-CONF) Results may be reported from either column if all calibration acceptance criteria as described in section 11are met

UNCONTROLLED COPY

13 3 2 Once the Aroclor pattern has been identified, compare the responses of 3 to 6 major peaks in the calibration standard of that Aroclor with the peaks observed in the sample extract The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 6 peaks and the calibration model selected in section 11 The concentration is determined using the 3 to 6 characteristic peaks and then the concentrations are averaged to determine the concentration of the Aroclor If there are interfering peaks with the 3 to 6 quantitation peaks that cause Aroclor average to be falsely overstated, then that interference peak is Q-deleted using the data system and the average is recalculated so that the average more truly represents the concentration in the sample This often occurs when there are more than one Aroclor in a sample extract or if pesticides are present Quantitation of mixed Aroclors will require the selection of peaks that are not shared in common by both Aroclors

13 3 3 For samples with severe matrix interferences, the quantitation may be performed by measuring the total area of the PCB pattern and quantifying on the basis of the Aroclor standard that is most similar to the sample Any peaks that are not identifiable as PCBs should be subtracted from the total area When the quantitation option is used, the sample problems should be described for the data user and quantification procedure documented

13 3 4 Using the data system calculate the concentration in the extract using the calibration model chosen for calibration (see the SOP SOC-CAL)

13 3 5 Using the data system, calculate the concentration of each analyte in the sample extract (Cex) μg/ml units using the calibration factor or calibration curve (Section 11) The sample concentration computed using the following equations

Aqueous Samples

$$Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$$

Where Cex = Concentration in extract in μg/ml
Vf = Final volume of extract in ml
D = Dilution factor
Vs = Volume of sample extracted, liters

UNCONTROLLED

Nonaqueous Samples

$$Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D) \times 1\ 000}{(W) \times 1\ 000}$$

Where Cex = Concentration in extract in μg/ml
Vf = Final volume of extract in ml
D = Dilution factor
W = Weight of sample extracted The wet or dry weight may be used, depending upon the specific client requirements

COPY

13 4 Sample concentrations are reported when all QC criteria for the analysis has been met or the results are qualified with a footnote

13 5 Data Review

Following primary data interpretation and calculations, all data is reviewed by a secondary analyst Following generation of the report, the report is also reviewed Refer to the SOP for Laboratory Data Review Process for details

13 6 Reporting

13 6 1 Reports are generated using the STEALTH Data Reporting System which compiles the SMO login information This compilation is then transferred to a file, which STEALTH uses to generate a report The forms generated may be CAS standard reports, DOD, or client-specific reports The compiled data from LIMS is also used to create EDDs

13 6 2 As an alternative reports are generated using Excel© templates located in R \SVG\forms The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements The detected analytes, surrogate and matrix spikes are then transferred, by hand or electronically to the templates

13 6 3 Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with an appropriate footnote For Arizona projects the appropriate Arizona qualifier must be used

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

UNCONTROLLED

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also, refer to the SOP for Nonconformity and Corrective Action for correct procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the SOP for Report Generation or in project specific requirements

15 METHOD PERFORMANCE

15 1 This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

COPY

15 2 The method detection limit (MDL) is established using the procedure described in the SOP for The Determination of Method Detection Limits (ADM-MDL) Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual

16 TRAINING

16 1 Training outline

16 1 1 Review literature (see references section) Read and understand the SOP Also review the applicable MSDS for all reagents and standards used Following these reviews, observe the procedure as performed by an experienced analyst at least three times

16 1 2 The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of 3 months During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst

16 1 3 Perform initial precision and recovery (IPR) study as described above for water samples Summaries of the IPR are reviewed and signed by the supervisor Copies may be forwarded to the employee's training file For applicable tests IPR studies should be performed in order to be equivalent to NELAC s Initial Demonstration of Capability

16 2 Training is documented following the SOP for Documentation of Technical Personnel Training

16 2 1 NOTE When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

UNCONTROLLED

17 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound feasibly possible, and within method requirements Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly

COPY

18 WASTE MANAGEMENT

The laboratory will comply with all Federal State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the laboratory Safety Manual Sections 6 and 7

19 REFERENCES

18 1 Polychlorinated Biphenyls (PCBs) as Aroclors, Method 8082 Revision 0 EPA Test Methods for Evaluating Solid Waste, SW-846, Final Update III, December 1996

18 2 EPASW846, Test Methods For Evaluating Solid Waste Third Edition, Update III December 1996, Method 8000B, Revision 2

18 3 8000C Method criteria, Arizona DHS, 2/13/2007 Available online at http //www azdhs gov/lab/license/tech/8000cmethod pdf

18 4 *DoD Quality Systems Manual for Environmental Laboratories* Version 4 1 4/22/09

UNCONTROLLED

20 CHANGES SINCE THE LAST REVISION

20 1 Sec 11 2 Removed SC and method 8000C reference
20 2 Sec 7 1 1 Removed HTRW prep requirements
20 3 Sec 11 2 Added DoD grand mean prohibition
20 4 Sec 11 2 2 Added TR window positioning step
20 5 Sec 11 2 5 Added DoD ICV criteria
20 6 Sec 11 3 2 Added DoD acceptance criteria
20 7 Sec 11 5 2 Added RT window positioning to CCV
20 8 Sec 12 3 Added DoD MB criteria
20 9 Sec 11 1 1 Changed ULL optimal amount form 2 L to 1 L

COPY

TABLE 1

Target Analytes, Method Reporting Limits, and Method Detection Limits

Aroclor	Water MRL (ug/L)	Water (low level) MRL (ug/L)	Water (ultra low level) MRL (ug/L)
Aroclor 1016	0 20	0 02	0 005
Aroclor 1221	0 40	0 04	0 01
Aroclor 1232	0 20	0 02	0 005
Aroclor 1242	0 20	0 02	0 005
Aroclor 1248	0 20	0 02	0 005
Aroclor 1254	0 20	0 02	0 005
Aroclor 1260	0 20	0 02	0 005

Aroclor	Soil/Sediment MRL (mg/kg)	Soil/Sediment (low level) MRL (ug/kg)
Aroclor 1016	0 10	10
Aroclor 1221	0 20	20
Aroclor 1232	0 10	10
Aroclor 1242	0 10	10
Aroclor 1248	0 10	10
Aroclor 1254	0 10	10
Aroclor 1260	0 10	10

Aroclor	Tissue MRL (ug/kg)
Aroclor 1016	10
Aroclor 1221	20
Aroclor 1232	10
Aroclor 1242	10
Aroclor 1248	10
Aroclor 1254	10
Aroclor 1260	10

UNCONTROLLED COPY

TABLE 2

Gas Chromatograph Operating Conditions*

Gas Chromatograph	Hewlett-Packard Model 5890 or equivalent w/ECD
Injection Port Temperature	300°C
Oven Temperature Program	160°C for 0 5 min, 30°/min ramp to 210°C, then 10°/min to 300°C hold 11 03 min
Detector Temperature	350°C
Injection Volume	1 µL
Column	30 m, DB-35MS and 30 m DB-XLB*
Carrier Gas	Helium
Auxillary Gas	Argon/Methane
Data System	HP Chemstation (acquisition) and Target (data)

UNCONTROLLED COPY

* The instrument temperatures may be modified depending on the instrument used Also, the GC column diameter and film thickness depend on the instrument used All conditions must be the same for initial calibration, continuing calibration, sample, and QC analyses

TABLE 3

CALIBRATION STANDARD PREPARATION

1016/1260 Initial Calibration Standards (prepared in hexane)

Aroclor 1016 50 ug/mL Intermediate	Aroclor 1260 50 ug/mL Intermediate	Surrogate 5 ug/mL Intermediate	Final Volume	Final Concentration Aroclors	Final Concentration Surrogates
12 5 uL	12 5 uL	12 5 uL	25 mL	25 ug/L	2 5 ug/L
25 uL	25 uL	25 uL	25 mL	50 ug/L	5 0 ug/L
250 uL	250 uL	250 uL	25 mL	500 ug/L	50 ug/L
500 uL	500 uL	500 uL	25 mL	1000 ug/L*	100 ug/L*
1000 uL	1000 uL	1000 uL	25 mL	2000 ug/L	200 ug/L
2500 uL	2500 uL	2500 uL	25 mL	5000 ug/L	500 ug/L

* CCV Standard

UNCONTROLLED

Single-Point Calibration Standards

Intermediate Standard (1000 ug/mL)	Aliquot	Final Volume	Solvent	Final Concentration
Aroclor 1221	25 uL	25 mL	Hexane	1000 ug/L
Aroclor 1232	25 uL	25 mL	↓	1000 ug/L
Aroclor 1242	25 uL	25 mL	↓	1000 ug/L
Aroclor 1248	25 uL	25 mL	↓	1000 ug/L
Aroclor 1254	25 uL	25 mL	↓	1000 ug/L
Aroclor 1262	25 uL	25 mL	↓	1000 ug/L
Aroclor 1268	25 uL	25 mL	↓	1000 ug/L

COPY

ICV Standards

ICV Stock Standard (100 ug/mL)	Aliquot	Final Volume	Solvent	Final Concentration
Aroclor 1016	250 uL	25 mL	Hexane	1000 ug/L
Aroclor 1221	250 uL	25 mL	↓	1000 ug/L
Aroclor 1232	250 uL	25 mL	↓	1000 ug/L
Aroclor 1242	250 uL	25 mL	↓	1000 ug/L
Aroclor 1248	250 uL	25 mL	↓	1000 ug/L
Aroclor 1254	250 uL	25 mL	↓	1000 ug/L
Aroclor 1260	250 uL	25 mL	↓	1000 ug/L
Aroclor 1262	250 uL	25 mL	↓	1000 ug/L
Aroclor 1268	250 uL	25 mL	↓	1000 ug/L

ATTACHMENT A

QC Acceptance Criteria
Method Reporting Limits
Method Detection Limits

UNCONTROLLED

COPY

Method Information

Method	8082	Source	SW-846	**Method ID**	MJ579
Prep	EPA 3535	Revision		Last User	AKamawal
Matrix	WATER	Level	LOW	Last Date	06/18/2009 11 30
Title	PCB Aroclors in Water				

Optimal Prep		
Sample Amount	1 000 00 m	0 00
Final Volume	2 00 ml	0 00

Hold Time	
Analytical	40 days from date Prep
Preparation	7 days from date Sampled

Require Confirmation?	YES
AFCEE ?	NO

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
2 2 4 4 5 5 -Hexabromobiphenyl	SURR				70-130		-		PERCE	100		59080-40 9
Aroclor 1016	MS		0 0094	0 2	10 161	30	32-115	30	ug/L	1000		12674 11-2
Aroclor 1016 {1}	MULTI		0 0094	0 2	10-161	30	32-115	30	ug/L	1000		CASID30221
Aroclor 1016 {2}	MULTI		0 0094	0 2	10-161	30	32-115	30	ug/L	1000		CASID30222
Aroclor 1016 {3}	MULTI		0 0094	0 2	10-161	30	32-115	30	ug/L	1000		CASID30223
Aroclor 1016 {4}	MULTI		0 0094	0 2	10-161	30	32-115	30	ug/L	1000		CASID30224
Aroclor 1016 {5}	MULTI		0 0094	0 2	10-161	30	32-115	30	ug/L	1000		CASID30225
Aroclor 1221	TRG		0 020	0 4	-		-		ug/L			11104-28-2
Aroclor 1221 {1}	MULTI		0 020	0 4			-		ug/L			CASID30226
Aroclor 1221 {2}	MULTI		0 020	0 4			-		ug/L			CASID30227
Aroclor 1221 {3}	MULTI		0 020	0 4					ug/L			CASID30228
Aroclor 1221 {4}	MULTI		0 020	0 4	-		-		ug/L			CASID30229
Aroclor 1221 {5}	MULTI		0 020	0 4	-		-		ug/L			CASID30230
Aroclor 1232	TRG		0 023	0 2			-		ug/L			11141 16-5
Aroclor 1232 {1}	MULTI		0 023	0 2			-		ug/L			CASID30231
Aroclor 1232 {2}	MULTI		0 023	0 2					ug/L			CASID30232
Aroclor 1232 {3}	MULTI		0 023	0 2					ug/L			CASID30233
Aroclor 1232 {4}	MULTI		0 023	0 2			-		ug/L			CASID30234
Aroclor 1232 {5}	MULTI		0 023	0 2			-		ug/L			CASID30235
Aroclor 1242	TRG		0 013	0 2			-		ug/L			53469-21 9
Aroclor 1242 {1}	MULTI		0 013	0 2			-		ug/L			CASID30236
Aroclor 1242 {2}	MULTI		0 013	0 2			-		ug/L			CASID30237
Aroclor 1242 {3}	MULTI		0 013	0 2			-		ug/L			CASID30238
Aroclor 1242 {4}	MULTI		0 013	0 2			-		ug/L			CASID30239
Aroclor 1242 {5}	MULTI		0 013	0 2			-		ug/L			CASID30240
Aroclor 1248	TRG		0 0054	0 2			-		ug/L			12672 29-6
Aroclor 1248 {1}	MULTI		0 0054	0 2	-		-		ug/L			CASID30241
Aroclor 1248 {2}	MULTI		0 0054	0 2			-		ug/L			CASID30242

CONFIDENTIAL

Method	8082	Source	SW-846	**Method ID**	MJ579
Prep	EPA 3535	Revision		Last User	AKamawal
Matrix	WATER	Level	LOW	Last Date	06/18/2009 11 30
Title	PCB Aroclors in Water				

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
Aroclor 1248 {3}	MULTI		0 0054	0 2	-		-		ug/L			CASID30243
Aroclor 1248 {4}	MULTI		0 0054	0 2			-		ug/L			CASID30244
Aroclor 1248 {5}	MULTI		0 0054	0 2					ug/L			CASID30245
Aroclor 1254	TRG		0 0070	0 2					ug/L			11097-69 1
Aroclor 1254 {1}	MULTI		0 0070	0 2			-		ug/L			CASID30246
Aroclor 1254 {2}	MULTI		0 0070	0 2			-		ug/L			CASID30247
Aroclor 1254 {3}	MULTI		0 0070	0 2	-				ug/L			CASID30248
Aroclor 1254 {4}	MULTI		0 0070	0 2			-		ug/L			CASID30249
Aroclor 1254 {5}	MULTI		0 0070	0 2			-		ug/L			CASID30250
Aroclor 1260	MS		0 0034	0 2	29 123	30	36-115	30	ug/L	1000		11096-82-5
Aroclor 1260 {1}	MULTI		0 0034	0 2	29-123	30	36-115	30	ug/L	1000		CASID30251
Aroclor 1260 {2}	MULTI		0 0034	0 2	29 123	30	36 115	30	ug/L	1000		CASID30252
Aroclor 1260 {3}	MULTI		0 0034	0 2	29-123	30	36-115	30	ug/L	1000		CASID30253
Aroclor 1260 {4}	MULTI		0 0034	0 2	29-123	30	36-115	30	ug/L	1000		CASID30254
Aroclor 1260 {5}	MULTI		0 0034	0 2	29 123	30	36-115	30	ug/L	1000		CASID30255
Aroclor 1262	TRG		0 0048	0 2	-		-		ug/L			37324-23 5
Aroclor 1262 {1}	MULTI		0 0048	0 2	-		-		ug/L			CASID30256
Aroclor 1262 {2}	MULTI		0 0048	0 2	-				ug/L			CASID30257
Aroclor 1262 {3}	MULTI		0 0048	0 2	-		-		ug/L			CASID30258
Aroclor 1262 {4}	MULTI		0 0048	0 2	-				ug/L			CASID30259
Aroclor 1262 {5}	MULTI		0 0048	0 2			-		ug/L			CASID30260
Aroclor 1268	TRG		0 0065	0 2			-		ug/L			11100 14-4
Aroclor 1268 {1}	MULTI		0 0065	0 2	-				ug/L			CASID30261
Aroclor 1268 {2}	MULTI		0 0065	0 2			-		ug/L			CASID30262
Aroclor 1268 {3}	MULTI		0 0065	0 2			-		ug/L			CASID30263
Aroclor 1268 {4}	MULTI		0 0065	0 2			-		ug/L			CASID30264
Aroclor 1268 {5}	MULTI		0 0065	0 2			-		ug/L			CASID30265
Decachlorobiphenyl	SURR				17 140		-		PERCE	100		2051 24 3
Tetrachloro m xylene	SURR				10-109		-		PERCE	100		877-09 8

DRAFT

Method Information

Method	8082	Source	SW-846	**Method ID**	MJ706
Prep	EPA 3535	Revision		Last User	AKamawal
Matrix	WATER	Level	LOW	Last Date	02/24/2009 14 44
Title	PCB-LL Aroclors in Water				

Optimal Prep		
Sample Amount.	1 000 00 m	0 00
Final Volume	2 00 ml	0 00

Hold Time	
Analytical	40 days from date Prep
Preparation	7 days from date Sampled

Require Confirmation?	YES
AFCEE ?	NO

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
2 2 4 4' 5 5 -Hexabromobiphenyl	SURR				70 130				PERCE	5		59080-40-9
Aroclor 1016	MS		0 0041	0 02	10 161	30	32-115	30	ug/L	100		12674-11 2
Aroclor 1016 {1}	MULTI		0 0041	0 02	10 161	30	32 115	30	ug/L	100		CASID30221
Aroclor 1016 {2}	MULTI		0 0041	0 02	10-161	30	32 115	30	ug/L	100		CASID30222
Aroclor 1016 {3}	MULTI		0 0041	0 02	10-161	30	32-115	30	ug/L	100		CASID30223
Aroclor 1016 {4}	MULTI		0 0041	0 02	10 161	30	32-115	30	ug/L	100		CASID30224
Aroclor 1016 {5}	MULTI		0 0041	0 02	10-161	30	32 115	30	ug/L	100		CASID30225
Aroclor 1221	TRG		0 0041	0 04	-		-		ug/L			11104 28 2
Aroclor 1221 {1}	MULTI		0 0041	0 04	-		-		ug/L			CASID30226
Aroclor 1221 {2}	MULTI		0 0041	0 04	-		-		ug/L			CASID30227
Aroclor 1221 {3}	MULTI		0 0041	0 04	-		-		ug/L			CASID30228
Aroclor 1221 {4}	MULTI		0 0041	0 04	-				ug/L			CASID30229
Aroclor 1221 {5}	MULTI		0 0041	0 04	-				ug/L			CASID30230
Aroclor 1232	TRG		0 0041	0 02			-		ug/L			11141-16-5
Aroclor 1232 {1}	MULTI		0 0041	0 02	-		-		ug/L			CASID30231
Aroclor 1232 {2}	MULTI		0 0041	0 02					ug/L			CASID30232
Aroclor 1232 {3}	MULTI		0 0041	0 02					ug/L			CASID30233
Aroclor 1232 {4}	MULTI		0 0041	0 02			-		ug/L			CASID30234
Aroclor 1232 {5}	MULTI		0 0041	0 02					ug/L			CASID30235
Aroclor 1242	TRG		0 0041	0 02			-		ug/L			53469-21-9
Aroclor 1242 {1}	MULTI		0 0041	0 02	-				ug/L			CASID30236
Aroclor 1242 {2}	MULTI		0 0041	0 02	-		-		ug/L			CASID30237
Aroclor 1242 {3}	MULTI		0 0041	0 02			-		ug/L			CASID30238
Aroclor 1242 {4}	MULTI		0 0041	0 02			-		ug/L			CASID30239
Aroclor 1242 {5}	MULTI		0 0041	0 02			-		ug/L			CASID30240
Aroclor 1248	TRG		0 0041	0 02			-		ug/L			12672-29-6
Aroclor 1248 {1}	MULTI		0 0041	0 02	-		-		ug/L			CASID30241
Aroclor 1248 {2}	MULTI		0 0041	0 02					ug/L			CASID30242

UNCONTROLLED

Method	8082	Source	SW-846	**Method ID**	MJ706
Prep	EPA 3535	Revision		Last User	AKamawal
Matrix	WATER	Level	LOW	Last Date	02/24/2009 14 44
Title	PCB-LL Aroclors in Water				

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
Aroclor 1248 {3}	MULTI		0 0041	0 02			-		ug/L			CASID30243
Aroclor 1248 {4}	MULTI		0 0041	0 02					ug/L			CASID30244
Aroclor 1248 {5}	MULTI		0 0041	0 02			-		ug/L			CASID30245
Aroclor 1254	TRG		0 0041	0 02			-		ug/L			11097-69 1
Aroclor 1254 {1}	MULTI		0 0041	0 02			-		ug/L			CASID30246
Aroclor 1254 {2}	MULTI		0 0041	0 02			-		ug/L			CASID30247
Aroclor 1254 {3}	MULTI		0 0041	0 02	-		-		ug/L			CASID30248
Aroclor 1254 {4}	MULTI		0 0041	0 02					ug/L			CASID30249
Aroclor 1254 {5}	MULTI		0 0041	0 02			-		ug/L			CASID30250
Aroclor 1260	MS		0 0041	0 02	29-123	30	36-115	30	ug/L	100		11096 82 5
Aroclor 1260 {1}	MULTI		0 0041	0 02	29-123	30	36-115	30	ug/L	100		CASID30251
Aroclor 1260 {2}	MULTI		0 0041	0 02	29-123	30	36-115	30	ug/L	100		CASID30252
Aroclor 1260 {3}	MULTI		0 0041	0 02	29-123	30	36-115	30	ug/L	100		CASID30253
Aroclor 1260 {4}	MULTI		0 0041	0 02	29-123	30	36-115	30	ug/L	100		CASID30254
Aroclor 1260 {5}	MULTI		0 0041	0 02	29 123	30	36-115	30	ug/L	100		CASID30255
Aroclor 1262	TRG		0 0041	0 02					ug/L			37324 23 5
Aroclor 1262 {1}	MULTI		0 0041	0 02	-		-		ug/L			CASID30256
Aroclor 1262 {2}	MULTI		0 0041	0 02	-		-		ug/L			CASID30257
Aroclor 1262 {3}	MULTI		0 0041	0 02	-		-		ug/L			CASID30258
Aroclor 1262 {4}	MULTI		0 0041	0 02	-		-		ug/L			CASID30259
Aroclor 1262 {5}	MULTI		0 0041	0 02			-		ug/L			CASID30260
Aroclor 1268	TRG		0 0041	0 02					ug/L			11100-14-4
Aroclor 1268 {1}	MULTI		0 0041	0 02					ug/L			CASID30261
Aroclor 1268 {2}	MULTI		0 0041	0 02			-		ug/L			CASID30262
Aroclor 1268 {3}	MULTI		0 0041	0 02					ug/L			CASID30263
Aroclor 1268 {4}	MULTI		0 0041	0 02			-		ug/L			CASID30264
Aroclor 1268 {5}	MULTI		0 0041	0 02			-		ug/L			CASID30265
Decachlorobiphenyl	SURR				17 140		-		PERCE	5		2051 24 3
PCBs Total	MS						-		ug/L	200		1336 36 3
Tetrachloro-m xylene	SURR				10 109		-		PERCE	5		877-09 8

DRAFT

Method Information

Method	8082	Source	SW-846	**Method ID**	MJ702
Prep	EPA 3535	Revision		Last User	AKamawal
Matrix	WATER	Level	LOW	Last Date	02/24/2009 14 44
Title	PCB Aroclors in UL-Water				

Optimal Prep		
Sample Amount	1 000 00 m	0 00
Final Volume	2 00 ml	0 00

Hold Time	
Analytical	40 days from date Prep
Preparation	7 days from date Sampled

Require Confirmation?	YES
AFCEE ?	NO

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
2 2 4 4 5 5 Hexabromobiphenyl	SURR				70 130				PERCE	5		59080-40-9
Aroclor 1016	MS		0 0041	0 005	10-161	30	32 115	30	ug/L	100		12674 11-2
Aroclor 1016 {1}	MULTI		0 0041	0 005	10 161	30	32 115	30	ug/L	100		CASID30221
Aroclor 1016 {2}	MULTI		0 0041	0 005	10 161	30	32 115	30	ug/L	100		CASID30222
Aroclor 1016 {3}	MULTI		0 0041	0 005	10 161	30	32 115	30	ug/L	100		CASID30223
Aroclor 1016 {4}	MULTI		0 0041	0 005	10 161	30	32 115	30	ug/L	100		CASID30224
Aroclor 1016 {5}	MULTI		0 0041	0 005	10 161	30	32 115	30	ug/L	100		CASID30225
Aroclor 1221	TRG		0 0041	0 010	-	30		30	ug/L			11104 28 2
Aroclor 1221 {1}	MULTI		0 0041	0 010	-	30		30	ug/L			CASID30226
Aroclor 1221 {2}	MULTI		0 0041	0 010		30		30	ug/L			CASID30227
Aroclor 1221 {3}	MULTI		0 0041	0 010		30		30	ug/L			CASID30228
Aroclor 1221 {4}	MULTI		0 0041	0 010	-	30	-	30	ug/L			CASID30229
Aroclor 1221 {5}	MULTI		0 0041	0 010	-	30		30	ug/L			CASID30230
Aroclor 1232	TRG		0 0041	0 005		30	-	30	ug/L			11141-16 5
Aroclor 1232 {1}	MULTI		0 0041	0 005	-	30	-	30	ug/L			CASID30231
Aroclor 1232 {2}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30232
Aroclor 1232 {3}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30233
Aroclor 1232 {4}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30234
Aroclor 1232 {5}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30235
Aroclor 1242	TRG		0 0041	0 005		30	-	30	ug/L			53469 21 9
Aroclor 1242 {1}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30236
Aroclor 1242 {2}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30237
Aroclor 1242 {3}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30238
Aroclor 1242 {4}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30239
Aroclor 1242 {5}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30240
Aroclor 1248	TRG		0 0041	0 005	-	30	-	30	ug/L			12672-29-6
Aroclor 1248 {1}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30241
Aroclor 1248 {2}	MULTI		0 0041	0 005		30		30	ug/L			CASID30242

UNCONTROLLED

Method	8082	Source	SW-846	**Method ID**	MJ702
Prep	EPA 3535	Revision		Last User	AKamawal
Matrix	WATER	Level	LOW	Last Date	02/24/2009 14 44
Title	PCB Aroclors in UL-Water				

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
Aroclor 1248 {3}	MULTI		0 0041	0 005		30		30	ug/L			CASID30243
Aroclor 1248 {4}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30244
Aroclor 1248 {5}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30245
Aroclor 1254	TRG		0 0041	0 005		30		30	ug/L			11097-69 1
Aroclor 1254 {1}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30246
Aroclor 1254 {2}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30247
Aroclor 1254 {3}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30248
Aroclor 1254 {4}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30249
Aroclor 1254 {5}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30250
Aroclor 1260	MS		0 0041	0 005	29 123	30	36-115	30	ug/L	100		11096 82 5
Aroclor 1260 {1}	MULTI		0 0041	0 005	29 123	30	36-115	30	ug/L	100		CASID30251
Aroclor 1260 {2}	MULTI		0 0041	0 005	29 123	30	36-115	30	ug/L	100		CASID30252
Aroclor 1260 {3}	MULTI		0 0041	0 005	29-123	30	36-115	30	ug/L	100		CASID30253
Aroclor 1260 {4}	MULTI		0 0041	0 005	29 123	30	36-115	30	ug/L	100		CASID30254
Aroclor 1260 {5}	MULTI		0 0041	0 005	29 123	30	36-115	30	ug/L	100		CASID30255
Aroclor 1262	TRG		0 0041	0 005		30		30	ug/L			37324 23 5
Aroclor 1262 {1}	MULTI		0 0041	0 005		30		30	ug/L			CASID30256
Aroclor 1262 {2}	MULTI		0 0041	0 005		30	-	30	ug/L			CASID30257
Aroclor 1262 {3}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30258
Aroclor 1262 {4}	MULTI		0 0041	0 005		30		30	ug/L			CASID30259
Aroclor 1262 {5}	MULTI		0 0041	0 005	-	30		30	ug/L			CASID30260
Aroclor 1268	TRG		0 0041	0 005		30		30	ug/L			11100-14-4
Aroclor 1268 {1}	MULTI		0 0041	0 005		30		30	ug/L			CASID30261
Aroclor 1268 {2}	MULTI		0 0041	0 005		30		30	ug/L			CASID30262
Aroclor 1268 {3}	MULTI		0 0041	0 005		30		30	ug/L			CASID30263
Aroclor 1268 {4}	MULTI		0 0041	0 005		30		30	ug/L			CASID30264
Aroclor 1268 {5}	MULTI		0 0041	0 005		30		30	ug/L			CASID30265
Decachlorobiphenyl	SURR				17 140				PERCE	5		2051-24 3
PCBs Total	MS								ug/L			1336 36 3
Tetrachloro m xylene	SURR				10-109				PERCE	5		877-09 8

Uncontrolled Document

Method Information

Method	8082	Source	SW-846	**Method ID**	MJ731
Prep	EPA 3541	Revision		Last User	AKamawal
Matrix	SOIL	Level	LOW	Last Date	05/05/2009 15 00
Title	Reg level 3541 PCB Aroclors in Soil				

Optimal Prep		
Sample Amount	10 00 g	0 00
Final Volume	10 00 ml	0 00

Hold Time	
Analytical	40 days from date Prep
Preparation	14 days from date Sampled

Require Confirmation?	YES
AFCEE ?	NO

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
2 2 4 4 5 5 Hexabromobiphenyl	SURR				70 130					100		59080-40 9
Aroclor 1016	MS		0 019	0 10	24 168	40	44-130	40	mg/Kg	1000		12674-11 2
Aroclor 1016 {1}	MULTI		0 019	0 10	24 168	40	44-130	40	mg/Kg	1000		CASID30221
Aroclor 1016 {2}	MULTI		0 019	0 10	24 168	40	44-130	40	mg/Kg	1000		CASID30222
Aroclor 1016 {3}	MULTI		0 019	0 10	24-168	40	44-130	40	mg/Kg	1000		CASID30223
Aroclor 1016 {4}	MULTI		0 019	0 10	24 168	40	44-130	40	mg/Kg	1000		CASID30224
Aroclor 1016 {5}	MULTI		0 019	0 10	24 168	40	44 130	40	mg/Kg	1000		CASID30225
Aroclor 1221	TRG		0 012	0 20		40	-	40	mg/Kg			11104-28-2
Aroclor 1221 {1}	MULTI		0 012	0 20		40	-	40	mg/Kg			CASID30226
Aroclor 1221 {2}	MULTI		0 012	0 20		40	-	40	mg/Kg			CASID30227
Aroclor 1221 {3}	MULTI		0 012	0 20		40	-	40	mg/Kg			CASID30228
Aroclor 1221 {4}	MULTI		0 012	0 20		40	-	40	mg/Kg			CASID30229
Aroclor 1221 {5}	MULTI		0 012	0 20		40	-	40	mg/Kg			CASID30230
Aroclor 1232	TRG		0 024	0 10		40	-	40	mg/Kg			11141-16-5
Aroclor 1232 {1}	MULTI		0 024	0 10	-	40	-	40	mg/Kg			CASID30231
Aroclor 1232 {2}	MULTI		0 024	0 10		40	-	40	mg/Kg			CASID30232
Aroclor 1232 {3}	MULTI		0 024	0 10		40	-	40	mg/Kg			CASID30233
Aroclor 1232 {4}	MULTI		0 024	0 10		40	-	40	mg/Kg			CASID30234
Aroclor 1232 {5}	MULTI		0 024	0 10		40	-	40	mg/Kg			CASID30235
Aroclor 1242	TRG		0 012	0 10		40	-	40	mg/Kg			53469-21-9
Aroclor 1242 {1}	MULTI		0 012	0 10	-	40	-	40	mg/Kg			CASID30236
Aroclor 1242 {2}	MULTI		0 012	0 10		40	-	40	mg/Kg			CASID30237
Aroclor 1242 {3}	MULTI		0 012	0 10		40	-	40	mg/Kg			CASID30238
Aroclor 1242 {4}	MULTI		0 012	0 10		40	-	40	mg/Kg			CASID30239
Aroclor 1242 {5}	MULTI		0 012	0 10		40	-	40	mg/Kg			CASID30240
Aroclor 1248	TRG		0 0072	0 10		40	-	40	mg/Kg			12672-29-6
Aroclor 1248 {1}	MULTI		0 0072	0 10	-	40	-	40	mg/Kg			CASID30241
Aroclor 1248 {2}	MULTI		0 0072	0 10		40		40	mg/Kg			CASID30242

CONFIDENTIAL

Method	8082	Source	SW-846	**Method ID**	MJ731
Prep	EPA 3541	Revision		Last User	AKamawal
Matrix	SOIL	Level	LOW	Last Date	05/05/2009 15 00
Title	Reg level 3541 PCB Aroclors in Soil				

Analyte Name	*Parm Type*	*Type*	*MDL*	*MRL*	*Surr/MS Limits*	*DMS RPD*	*LCS Limits*	*DLCS RPD*	*Units*	*Spike Level*	*Reg Limit*	*Analyte ID*
Aroclor 1248 {3}	MULTI		0 0072	0 10		40		40	mg/Kg			CASID30243
Aroclor 1248 {4}	MULTI		0 0072	0 10		40		40	mg/Kg			CASID30244
Aroclor 1248 {5}	MULTI		0 0072	0 10		40	-	40	mg/Kg			CASID30245
Aroclor 1254	TRG		0 0088	0 10		40		40	mg/Kg			11097 69 1
Aroclor 1254 {1}	MULTI		0 0088	0 10		40	-	40	mg/Kg			CASID30246
Aroclor 1254 {2}	MULTI		0 0088	0 10		40		40	mg/Kg			CASID30247
Aroclor 1254 {3}	MULTI		0 0088	0 10		40	-	40	mg/Kg			CASID30248
Aroclor 1254 {4}	MULTI		0 0088	0 10		40		40	mg/Kg			CASID30249
Aroclor 1254 {5}	MULTI		0 0088	0 10		40		40	mg/Kg			CASID30250
Aroclor 1260	MS		0 013	0 10	24 163	40	52-127	40	mg/Kg	1000		11096 82 5
Aroclor 1260 {1}	MULTI		0 013	0 10	24-163	40	52-127	40	mg/Kg	1000		CASID30251
Aroclor 1260 {2}	MULTI		0 013	0 10	24 163	40	52-127	40	mg/Kg	1000		CASID30252
Aroclor 1260 {3}	MULTI		0 013	0 10	24 163	40	52-127	40	mg/Kg	1000		CASID30253
Aroclor 1260 {4}	MULTI		0 013	0 10	24-163	40	52 127	40	mg/Kg	1000		CASID30254
Aroclor 1260 {5}	MULTI		0 013	0 10	24-163	40	52-127	40	mg/Kg	1000		CASID30255
Aroclor 1262	TRG		0 020	0 10		40		40	mg/Kg			37324 23-5
Aroclor 1262 {1}	MULTI		0 020	0 10		40		40	mg/Kg			CASID30256
Aroclor 1262 {2}	MULTI		0 020	0 10	-	40		40	mg/Kg			CASID30257
Aroclor 1262 {3}	MULTI		0 020	0 10		40		40	mg/Kg			CASID30258
Aroclor 1262 {4}	MULTI		0 020	0 10		40		40	mg/Kg			CASID30259
Aroclor 1262 {5}	MULTI		0 020	0 10		40		40	mg/Kg			CASID30260
Aroclor 1268	TRG		0 0066	0 10		40		40	mg/Kg			11100 14-4
Aroclor 1268 {1}	MULTI		0 0066	0 10		40		40	mg/Kg			CASID30261
Aroclor 1268 {2}	MULTI		0 0066	0 10		40		40	mg/Kg			CASID30262
Aroclor 1268 {3}	MULTI		0 0066	0 10		40		40	mg/Kg			CASID30263
Aroclor 1268 {4}	MULTI		0 0066	0 10		40		40	mg/Kg			CASID30264
Aroclor 1268 {5}	MULTI		0 0066	0 10		40		40	mg/Kg			CASID30265
Decachlorobiphenyl	SURR				38 144				PERCE	100		2051 24 3
Tetrachloro-m-xylene	SURR				22 130				PERCE	100		877-09 8

UNCONTROLLED COPY

Method Information

Method	8082	Source	SW-846	**Method ID**	MJ696
Prep	EPA 3541	Revision		Last User	AKamawal
Matrix	SOIL	Level	LOW	Last Date	04/03/2008 17 42
Title	PCB Aroclors in LL-Sediment/Soil				

Optimal Prep		
Sample Amount	20 00 g	0 00
Final Volume	4 00 ml	0 00

Hold Time	
Analytical	40 days from date Prep
Preparation	14 days from date Sampled

Require Confirmation?	YES
AFCEE ?	NO

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
2 2 4 4 6 6 Hexabromobiphenyl	SURR				70 130				PERCE	100		59261-08-4
Aroclor 1016	MS		2 1	10	24-168	40	44 130	40	ug/Kg	1000		12674-11 2
Aroclor 1016 {1}	MULTI		2 1	10	24-168	40	44-130	40	ug/Kg	1000		CASID30221
Aroclor 1016 {2}	MULTI		2 1	10	24 168	40	44-130	40	ug/Kg	1000		CASID30222
Aroclor 1016 {3}	MULTI		2 1	10	24-168	40	44-130	40	ug/Kg	1000		CASID30223
Aroclor 1016 {4}	MULTI		2 1	10	24 168	40	44-130	40	ug/Kg	1000		CASID30224
Aroclor 1016 {5}	MULTI		2 1	10	24-168	40	44-130	40	ug/Kg	1000		CASID30225
Aroclor 1221	TRG		2 1	20		40	-		ug/Kg			11104-28-2
Aroclor 1221 {1}	MULTI		2 1	20	-	40	-		ug/Kg			CASID30226
Aroclor 1221 {2}	MULTI		2 1	20		40			ug/Kg			CASID30227
Aroclor 1221 {3}	MULTI		2 1	20	-	40	-		ug/Kg			CASID30228
Aroclor 1221 {4}	MULTI		2 1	20	-	40			ug/Kg			CASID30229
Aroclor 1221 {5}	MULTI		2 1	20	-	40			ug/Kg			CASID30230
Aroclor 1232	TRG		2 1	10	-	40	-		ug/Kg			11141-16 5
Aroclor 1232 {1}	MULTI		2 1	10	-	40	-		ug/Kg			CASID30231
Aroclor 1232 {2}	MULTI		2 1	10	-	40	-		ug/Kg			CASID30232
Aroclor 1232 {3}	MULTI		2 1	10	-	40	-		ug/Kg			CASID30233
Aroclor 1232 {4}	MULTI		2 1	10		40	-		ug/Kg			CASID30234
Aroclor 1232 {5}	MULTI		2 1	10	-	40			ug/Kg			CASID30235
Aroclor 1242	TRG		2 1	10	-	40	-		ug/Kg			53469-21 9
Aroclor 1242 {1}	MULTI		2 1	10	-	40	-		ug/Kg			CASID30236
Aroclor 1242 {2}	MULTI		2 1	10		40	-		ug/Kg			CASID30237
Aroclor 1242 {3}	MULTI		2 1	10		40	-		ug/Kg			CASID30238
Aroclor 1242 {4}	MULTI		2 1	10		40	-		ug/Kg			CASID30239
Aroclor 1242 {5}	MULTI		2 1	10	-	40	-		ug/Kg			CASID30240
Aroclor 1248	TRG		2 1	10	-	40	-		ug/Kg			12672-29-6
Aroclor 1248 {1}	MULTI		2 1	10	-	40			ug/Kg			CASID30241
Aroclor 1248 {2}	MULTI		2 1	10	-	40			ug/Kg			CASID30242

UNOFFICIAL COPY

Method 8082
Prep EPA 3541
Matrix SOIL
Title PCB Aroclors in LL-Sediment/Soil

Source SW-846
Revision
Level LOW

Method ID MJ696
Last User AKamawal
Last Date 04/03/2008 17 42

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
Aroclor 1248 {3}	MULTI		2 1	10		40	-		ug/Kg			CASID30243
Aroclor 1248 {4}	MULTI		2 1	10		40	-		ug/Kg			CASID30244
Aroclor 1248 {5}	MULTI		2 1	10		40			ug/Kg			CASID30245
Aroclor 1254	TRG		2 1	10		40			ug/Kg			11097-69 1
Aroclor 1254 {1}	MULTI		2 1	10		40			ug/Kg			CASID30246
Aroclor 1254 {2}	MULTI		2 1	10		40	-		ug/Kg			CASID30247
Aroclor 1254 {3}	MULTI		2 1	10		40			ug/Kg			CASID30248
Aroclor 1254 {4}	MULTI		2 1	10	-	40			ug/Kg			CASID30249
Aroclor 1254 {5}	MULTI		2 1	10	-	40	-		ug/Kg			CASID30250
Aroclor 1260	MS		2 1	10	24-163	40	52-127	40	ug/Kg	1000		11096 82 5
Aroclor 1260 {1}	MULTI		2 1	10	24 163	40	52 127	40	ug/Kg	1000		CASID30251
Aroclor 1260 {2}	MULTI		2 1	10	24 163	40	52 127	40	ug/Kg	1000		CASID30252
Aroclor 1260 {3}	MULTI		2 1	10	24 163	40	52-127	40	ug/Kg	1000		CASID30253
Aroclor 1260 {4}	MULTI		2 1	10	24 163	40	52-127	40	ug/Kg	1000		CASID30254
Aroclor 1260 {5}	MULTI		2 1	10	24 163	40	52-127	40	ug/Kg	1000		CASID30255
Aroclor 1262	TRG		2 1	10		40	-		ug/Kg			37324-23 5
Aroclor 1262 {1}	MULTI		2 1	10		40	-		ug/Kg			CASID30256
Aroclor 1262 {2}	MULTI		2 1	10		40			ug/Kg			CASID30257
Aroclor 1262 {3}	MULTI		2 1	10		40	-		ug/Kg			CASID30258
Aroclor 1262 {4}	MULTI		2 1	10	-	40			ug/Kg			CASID30259
Aroclor 1262 {5}	MULTI		2 1	10		40	-		ug/Kg			CASID30260
Aroclor 1268	TRG		2 1	10		40	-		ug/Kg			11100-14-4
Aroclor 1268 {1}	MULTI		2 1	10		40			ug/Kg			CASID30261
Aroclor 1268 {2}	MULTI		2 1	10		40	-		ug/Kg			CASID30262
Aroclor 1268 {3}	MULTI		2 1	10		40			ug/Kg			CASID30263
Aroclor 1268 {4}	MULTI		2 1	10		40	-		ug/Kg			CASID30264
Aroclor 1268 {5}	MULTI		2 1	10		40	-		ug/Kg			CASID30265
Decachlorobiphenyl	SURR				38 144		-		PERCE	100		2051 24 3
PCBs, Total	MS						-		ug/Kg	2000		1336 36 3
Tetrachloro-m xylene	SURR				22-130		-		PERCE	100		877-09-8

UNCONTROLLED COPY

Method Information

Method	8082	Source	SW-846	**Method ID**	MJ923
Prep	EPA 3541	Revision		Last User	AKamawal
Matrix	TISSUE	Level	LOW	Last Date	04/03/2008 17 51
Title	EPS PCB Aroclors in Tissue				

Optimal Prep		
Sample Amount	10 00 g	0 00
Final Volume	2 00 ml	0 00

Hold Time	
Analytical	40 days from date Prep
Preparation	365 days from date Sample

Require Confirmation?	YES
AFCEE ?	NO

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
2 2 4 4 5 5 -Hexabromobiphenyl	SURR				70 130				PERCE	100		59080-40-9
2 2' 4 4 6 6 Hexabromobiphenyl	SURR				70 130		-		PERCE	100		59261-08-4
Aroclor 1016	MS		1 7	10	10 165	40	42-128	40	ug/Kg	1000		12674 11-2
Aroclor 1016 {1}	MULTI		1 7	10	10 165	40	42-128	40	ug/Kg	1000		CASID30221
Aroclor 1016 {2}	MULTI		1 7	10	10 165	40	42-128	40	ug/Kg	1000		CASID30222
Aroclor 1016 {3}	MULTI		1 7	10	10 165	40	42-128	40	ug/Kg	1000		CASID30223
Aroclor 1016 {4}	MULTI		1 7	10	10 165	40	42-128	40	ug/Kg	1000		CASID30224
Aroclor 1016 {5}	MULTI		1 7	10	10 165	40	42 128	40	ug/Kg	1000		CASID30225
Aroclor 1221	TRG		1 7	20		40	-	40	ug/Kg			11104-28 2
Aroclor 1221 {1}	MULTI		1 7	20		40	-	40	ug/Kg		CASID30	CASID30226
Aroclor 1221 {2}	MULTI		1 7	20	-	40	-	40	ug/Kg		CASID30	CASID30227
Aroclor 1221 {3}	MULTI		1 7	20		40	-	40	ug/Kg		CASID30	CASID30228
Aroclor 1221 {4}	MULTI		1 7	20		40	-	40	ug/Kg		CASID30	CASID30229
Aroclor 1221 {5}	MULTI		1 7	20		40	-	40	ug/Kg		CASID30	CASID30230
Aroclor 1232	TRG		1 7	10		40	-	40	ug/Kg			11141 16 5
Aroclor 1232 {1}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30231
Aroclor 1232 {2}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30232
Aroclor 1232 {3}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30233
Aroclor 1232 {4}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30234
Aroclor 1232 {5}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30235
Aroclor 1242	TRG		1 7	10		40	-	40	ug/Kg			53469-21 9
Aroclor 1242 {1}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30236
Aroclor 1242 {2}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30237
Aroclor 1242 {3}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30238
Aroclor 1242 {4}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30239
Aroclor 1242 {5}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30240
Aroclor 1248	TRG		1 7	10		40	-	40	ug/Kg			12672 29-6
Aroclor 1248 {1}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30241

CONFIDENTIAL PROPERTY OF

Method	8082	Source	SW-846	**Method ID**	MJ923
Prep	EPA 3541	Revision		Last User	AKamawal
Matrix	TISSUE	Level	LOW	Last Date	04/03/2008 17 51
Title	EPS PCB Aroclors in Tissue				

Analyte Name	Parm Type	Type	MDL	MRL	Surr/MS Limits	DMS RPD	LCS Limits	DLCS RPD	Units	Spike Level	Reg Limit	Analyte ID
Aroclor 1248 {2}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30242
Aroclor 1248 {3}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30243
Aroclor 1248 {4}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30244
Aroclor 1248 {5}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30245
Aroclor 1254	TRG		1 7	10	-	40	-	40	ug/Kg			11097-69 1
Aroclor 1254 {1}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30246
Aroclor 1254 {2}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30247
Aroclor 1254 {3}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30248
Aroclor 1254 {4}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30249
Aroclor 1254 {5}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30250
Aroclor 1260	MS		1 7	10	10-185	40	46 131	40	ug/Kg	1000		11096 82 5
Aroclor 1260 {1}	MULTI		1 7	10	10-185	40	46-131	40	ug/Kg	1000		CASID30251
Aroclor 1260 {2}	MULTI		1 7	10	10 185	40	46-131	40	ug/Kg	1000		CASID30252
Aroclor 1260 {3}	MULTI		1 7	10	10-185	40	46 131	40	ug/Kg	1000		CASID30253
Aroclor 1260 {4}	MULTI		1 7	10	10-185	40	46-131	40	ug/Kg	1000		CASID30254
Aroclor 1260 {5}	MULTI		1 7	10	10-185	40	46 131	40	ug/Kg	1000		CASID30255
Aroclor 1262	TRG		1 7	10		40	-	40	ug/Kg			37324-23 5
Aroclor 1262 {1}	MULTI		1 7	10		40	-	40	ug/Kg		CASID30	CASID30256
Aroclor 1262 {2}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30257
Aroclor 1262 {3}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30258
Aroclor 1262 {4}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30259
Aroclor 1262 {5}	MULTI		1 7	10	-	40	-	40	ug/Kg		CASID30	CASID30260
Aroclor 1268	MS		1 7	10	70 130	40	70-130	40	ug/Kg	1000		11100 14-4
Aroclor 1268 {1}	MULTI		1 7	10		40	-	40	ug/Kg	1000	CASID30	CASID30261
Aroclor 1268 {2}	MULTI		1 7	10		40	-	40	ug/Kg	1000	CASID30	CASID30262
Aroclor 1268 {3}	MULTI		1 7	10	-	40	-	40	ug/Kg	1000	CASID30	CASID30263
Aroclor 1268 {4}	MULTI		1 7	10		40	-	40	ug/Kg	1000	CASID30	CASID30264
Aroclor 1268 {5}	MULTI		1 7	10		40	-	40	ug/Kg	1000	CASID30	CASID30265
Decachlorobiphenyl	SURR				10-202		-		PERCE	100		2051 24 3
Tetrachloro-m-xylene	SURR				17-118		-		PERCE	100		877-09-8

CONTROLLED

STANDARD OPERATING PROCEDURE

WASTE DILUTION EXTRACTION

EXT-3580

Revision 2

April 30, 2007

UNCONTROLLED

Approved By _____ Supervisor _____ Date 5/1/07

_____ QA Manager _____ Date 5-1-07

_____ Laboratory Manager _____ Date 5/1/07

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2007

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

WASTE DILUTION EXTRACTION

1 SCOPE AND APPLICATION

1 1 This procedure uses techniques described in EPA Method 3580A for performing waste dilution for determination of nonvolatile and semi volatile organic compounds using various chromatographic procedures

1 2 This method is applicable to non-aqueous liquid wastes that are miscible in the specified organic solvent

UNCONTROLLED

2 SUMMARY OF METHOD

The waste sample is diluted in an appropriate organic solvent The solution is dried and concentrated if necessary Depending on the determinative procedure, a cleanup step may be employed

3 DEFINITIONS

COPY

3 1 Laboratory Control Sample (LCS) - A laboratory blank that has been fortified with target analyte and used to determine that the analysis is in control

3 2 Matrix Spike (MS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis The percent recovery is calculated The MS is used to evaluate the effects of the sample matrix on the method used for the analysis The concentration of the spike should be at three to five times the sample result or at levels specified by a project analysis plan

3 3 Duplicate Sample (DUP) - A laboratory duplicate The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper The relative percent difference between the samples is calculated and used to assess analytical precision

3 4 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free matrix and is designed to monitor the introduction of artifacts into the analytical process The method blank is carried through the entire analytical procedure

4 INTERFERENCES

4 1 Phthalate esters can pose difficulties when performing sample extractions for organochlorine pesticides PCBs and other semi-volatile organics Phthalates are easily

extracted or leached from materials containing plastics during laboratory operations Interferences from phthalates can best be minimized by avoiding contact with any plastic materials

4 2 Since the analysis deals with high-concentration wastes, waste solvents, oils, etc, care must be taken to avoid cross contamination and contamination of apparatus All apparatus must be cleaned before and after use

4 3 Refer to Method 3500B for additional discussion of interferences

5 SAFETY

UNCONTROLLED

5 1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves

5 2 Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available Refer to the CAS Environmental Health and Safety Manual and the appropriate MSDS prior to beginning this method

5 3 This method uses Methylene Chloride, a known human carcinogen Viton brand gloves should be used while rinsing, pouring or transferring the solvent

COPY

6 RESPONSIBILITIES

It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

7 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the applicable section in the analytical method or SOP for collection, preservation, and holding times

8 APPARATUS AND MATERIALS

8 1 Kuderna-Danish (K-D) apparatus

8 1 1 Concentrator tube - 10 ml, graduated (Kontes K-570050 1025 or equivalent) and attachment springs or clips

8 1 2 Evaporation flask - 500 ml (Kontes K570001-500 or equivalent) Attach to concentrator tube with springs, clamps or equivalent

8 1 3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent)

8 2 Boiling chips - Pre-cleaned approximately 10/40 mesh (silicon carbide or equivalent)

8 3 S-Evap - Heated, capable of temperature control (± 5°C) The bath should be used in a hood

8 4 N-Evap concentrator

UNCONTROLLED

8 5 Vortex mixer

8 6 Volumetric flasks, Class A, 10mL

8 7 Culture tubes, disposable, 20mL

8 8 Vials - Glass, 2 ml capacity, with Teflon lined screw or crimp top

8 9 Disposable glass pasteur pipets and bulb

COPY

8 10 Graduated pipets, various volumes

8 11 Analytical balance - 0 001 g

8 12 Glass scintillation vials, 20mL, with Teflon or aluminum lined caps

9 REAGENTS

9 1 Reagent grade chemicals shall be used in all tests Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination

9 2 Sodium sulfate (granular, anhydrous), Na_2SO_4 Purify by heating at 400°C for 4 hours

9 3 Concentrated Sulfuric acid

9 4 Solvents

9 4 1 Methylene chloride (DCM), pesticide quality or equivalent

9 4 2 Hexane, pesticide quality or equivalent

9 4 3 Acetone, pesticide quality or equivalent

9 4 4 Methanol, pesticide quality or equivalent

10 PREVENTIVE MAINTENANCE

Routine cleaning of the apparatus used is necessary, especially parts exposed to contact with samples

11 PROCEDURE

UNCONTROLLED

11 1 Record all extraction and sample information on the applicable benchsheet See Attachment A for example benchsheets

11 2 Semivolatile organics (GC/MS, GC, PHC)

11 2 1 Weigh out 1 0 gram of sample (use Na2SO4 for the MB) into a 10ml volumetric flask Record weight to the nearest 0 01g If disposable glassware is preferred, pipet 10 o mL of solvent into scintillation vials and mark the meniscus, discard the solvent

COPY

11 2 2 Add the appropriate surrogate and matrix spike solutions (see benchsheet)

11 2 3 Dilute to 10ml F V with the appropriate solvent for the analysis, vortex and transfer into a test tube

11 2 4 To remove any water present in the sample, add 2 grams of anhydrous Na2SO4 and vortex for 1 minute Continue to the applicable section below

11 2 5 GC/PHC Analyses

11 2 5 1 Dilute 1ml of sample to 10ml in DCM (1 10 dilution)

11 2 5 2 Transfer 1ml to a labeled autosampler vial for analysis and store the remainder

11 2 6 GC/MS Analyses

11 2 6 1 Dilute 2mls of sample to 10mls in DCM (1 5 dilution) Filter and prepare dilution for GPC Transfer remaining extract into a test tube or GPC tube Store original 10ml volume in refrigerator

11 2 6 2 Do GPC cleanup (see CAS SOP)

11 2 6 3 Concentrate the extracts on an S-Evap with the temperature set between 70-75°C Record temperature Remove the KD when the solvent level is low enough to remove the collector Extreme caution must be used to ensure that the sample does not concentrate too low or to dryness

11 2 6 4 Concentrate the extracts to <0 5ml on the N-Evap under a gentle stream of nitrogen with the temperature not exceeding 35°C

11 2 6 5 Extreme caution must be used to ensure that the sample does not concentrate too low or to dryness

UNCONTROLLED

11 2 6 6 Bring extract to 0 5ml F V in DCM

11 2 6 7 Place in a labeled, clear 2ml autosampler vial. Do FID screening. (See CAS SOP)

11 2 7 Complete all necessary paperwork and benchsheet review checklist Turn extracts and paperwork over to analysts

11 3 PCBs in oil

11 3 1 Weigh out 0 5 g of sample into a small culture tube Record weight to the nearest 0 01 g Use same amount of oil for the method blank and laboratory control sample

COPY

11 3 2 Add surrogate and matrix spikes as necessary

11 3 3 Add 10 mL of hexane and vortex

11 3 4 Transfer 4 mL of extract to another small culture tube Perform an H_2SO_4 cleanup (see SOP SOC 3665) on samples and QC Archive the remaining extract

11 3 5 Quantitatively transfer the cleaned extract to another small culture tube Place 0 5g of Florisil powder into each sample Vortex for 10-15 seconds and allow to sit overnight Perform the cleanup on QC extracts as well

11 3 6 If a 2 ml aliquot was cleaned up, take back to 2 mL final volume on N-evap

11 3 7 Place in a 2-mL green vial mark level on vial, label and store extra extract Do not get any H2SO4 in the vial

11 4 Pesticides/PCBs in oil

11 4 1 Weigh out 1 g of the sample into a 10 mL volumetric flask Record weight to the nearest 0 01 g Use the same amount of oil for the laboratory control sample, and solvent only for the method blank

11 4 2 Add surrogate and matrix spike solution Use the same amount as used in the soil extractions

11 4 3 Dilute to 10 ml with methylene chloride, vortex and pour into a 20 ml disposable tube This is final volume

11 4 4 Add 2 g of muffled anhydrous sodium sulfate to sample and vortex for two minutes

UNCONTROLLED

11 4 5 For GPC cleanup refer to CAS SOP SOC-3640A. Once samples are at 10 ml in DCM, the GPC analyst takes 4mls off and brings it up to 10ml.

11 4 6 After GPC, concentrate the extract on the S-Evap, keeping the temperature between 60-75°C Concentrate to approximately 5 ml and remove from the S-Evap, cool, and add approximately 10mL of hexane Return to the S-Evap and concentrate until solvent stops dripping

11 4 7 Take to 2 ml final volume in hexane for a 10 ml calculated final volume Do a Sulfuric acid cleanup on 1 ml of the extract and put it in a green vial for PCB analysis Put the other 1 ml in a yellow vial for Pesticides analysis Mark level on vials

COPY

12 QUALITY CONTROL

12 1 Refer to the SOP for the determinative method and SOP for Sample Batches for minimum QC requirements

12 2 Any reagent blanks, laboratory control samples or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples

13 CORRECTIVE ACTION

13 1 Refer to the SOP for *Nonconformity and Corrective Action* for procedures for corrective action Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected

13 2 Handling out-of-control or unacceptable data

13 2 1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks runlogs for example

13 2 2 Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when a) corrective action is not taken or not possible b) corrective action fails to correct an out-of-control problem on a laboratory QC or calibration analysis c) reanalysis corrects the nonconformity but is not a procedurally compliant analysis

14 POLLUTION PREVENTION

UNCONTROLLED

It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly

15 WASTE MANAGEMENT

15 1 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the laboratory Safety Manual Sections 6 and 7

COPY

15 2 This method uses Methylene Chloride and any waste generated from this solvent must be placed in the collection cans in the lab The solvent will then be added to the hazardous waste storage area and recycled off site

15 3 This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations

16 METHOD PERFORMANCE

Available method performance data is given in the reference method In addition this procedure was validated through single laboratory studies of accuracy and precision as specified in the determinative procedures

17 TRAINING

17 1 Training outline

17 1 1 Review literature (see references section) Read and understand the SOP Also review the applicable MSDS for all reagents and standards used Following these reviews, observe the procedure as performed by an experienced analyst at least three times

17 1 2 The next training step is to assist in the procedure under the guidance of an experienced analyst During this period the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst

17 1 3 Perform initial precision and recovery (IPR) study as described above for water samples Summaries of the IPR are reviewed and signed by the supervisor Copies may be forwarded to the employee's training file For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability

UNCONTROLLED

17 2 Training is documented following the SOP *for Documentation of Technical Personnel Training*

NOTE When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently

COPY

18 REFERENCES

Waste Dilution EPASW846, "Test Methods For Evaluating Solid Waste", Update I, July 1992 Method 3580A, Revision 1

Attachment A

Benchsheets

UNCONTROLLED

COPY

Additional Prep Information For PCB By Method 3580

Service Request #_____ Work Group # PCB _____

Solvents/Reagents used

Hexane Lot #_____ Other _____

Cleanups

Sulfuric Acid Clean-up (3665)_____ ☐ all samples ☐ some samples._____

Florisil Clean-up (3620)_____ ☐ all samples ☐ some samples _____

Additional Clean-up _____ ☐ all samples ☐ some samples _____

PCB Vial _____ Vial Storage _____

Archived Extract Storage _____

UNCONTROLLED

Comments/Observations _____

_____

_____

_____

_____

_____

_____

_____

COPY

Bench Sheet Review Check List
☐ Hold Times Met (if no, Reason _____)
☐ Prep date, dept, method, product code correct in stealth
☐ Spike Information correct
☐ Weights/Volumes and units correct on raw and final bench sheets
☐ Sample IDs have been checked—Bottle numbers appended if required
☐ Names present for Started by, Completed by, relinquished by, and witnessed by
☐ Training has been circled
☐ Extract Storage recorded
☐ Additional Prep Sheet completely filled out (NA or line out Blanks)
☐ All clean ups have been noted on additional prep sheet
☐ Signed service request with Form V, if applicable, has been attached

EXTRACTION PROCEDURE FOR

PCBs IN OIL

EPA Method 3580A

1 Weigh out 0 5 g of sample into a small culture tube Record weight to the nearest 0 01 g Use same amount of oil for the method blank and laboratory control sample

2 Add surrogate and matrix spikes as necessary

3 Add 10 mL of hexane and vortex

4 Place 4 mL of solution from step 3 in another small culture tube Add 4 mL concentrated H_2SO_4 and vortex Let the phases separate and if necessary centrifuge the sample to remove all H_2SO_4 from organic layer If no unresolvable emulsion forms, but the top extract layer is cloudy or dark pull off the top layer and do another acid clean up with another 4 mLs concentrated H_2SO_4

UNCONTROLLED

5 If the centrifuge does not break up the emulsion, do a florisil clean up on a 2 mLs (non-acid cleaned up) aliquot of the solution from step 3 If a Florisil clean up is done on a sample then a Florisil clean up must be done on 2 mLs of the method blank (There must be two vials for method blanks--one that has had a Florisil cleanup and one that has not. Be sure to label each vial appropriately)

> **Florisil clean up** Set up columns on manifold add 1/4 inch powdered sulfate to columns rinse columns with 10mL of hexane and discard hexane Load sample onto column elute with 5 mL of hexane and collect. If a 2 ml aliquot was cleaned up take back to 2 mL final volume on N-evap

6 Place in a 2-mL green vial mark level on vial label and store extra extract. **Do not get any H_2SO_4 in vial**

COPY

Approved By/Date
5-22 01
Extraction Manager
5-14 01
Instrument Manager
Sal Coordinator

Additional Prep Information For EPA 3580

Service Request _____ **Workgroup** _____

Start (Time/Date/Initial) _____

Pipette Lot # _____ DCM Lot # _____

S-Evap Temp _____ N-evap Temp _____

Clean-up #1 _____ Initial/Date _____

Clean-up #2 _____ Initial/Date _____

Extract Storage _____

Date Completed _____

UNCONTROLLED

Comments/Observations

_____

_____

_____

_____

_____

_____

_____

COPY

Bench Sheet Review Check List
☐ Hold Times Met (If no, Reason _____)
☐ Prep date, dept, method, product code correct in stealth
☐ Spike Information correct
☐ Weights/Volumes and units correct on raw and final bench sheets
☐ Sample IDs have been checked—Bottle numbers appended if required
☐ Names present for Started by, Completed by, relinquished by, and witnessed by
☐ Training has been circled
☐ Extract Storage recorded
☐ Additional Prep Sheet completely filled out (NA or line out Blanks)
☐ All clean-ups have been noted on additional prep sheet
☐ Signed service request with Form V, if applicable, has been attached

COLUMBIA ANALYTICAL SERVICES, INC
STANDARD OPERATING PROCEDURE FOR
Extracting Base Neutral and Acid Semi-Volatile Compounds by 8270C in Oil
Method 3580A

Procedure

Note a) **All anhydrous sodium sulfate (Na_2SO_4) used in this procedure must be thoroughly rinsed with methylene chloride (DCM)**

1 Weigh out 1 0 gram of sample (use Na_2SO_4 ª for the MB) into a 10ml volumetric flask Record weight to the nearest 0 01g

2 Add surrogate and matrix spike solutions (see chart below)

3 Dilute to a 10ml Xtm. F V in DCM vortex and transfer into a test tube

4 To remove any water present in the sample add 2 grams of anhydrous Na_2SO_4 ª and vortex for 1 minute

5 Dilute 2mls of sample to 10mls in DCM (1 5 dilution) Filter and prepare dilution for GPC Transfer remaining extract into a test tube or GPC tube Store original 10ml volume in refrigerator

6 Do GPC cleanup. (see CAS SOP)

7 Concentrate the extracts on an S-Evap with the temperature set between 70 75 °C. Record temperature Remove the KD when the solvent level is low enough to remove the collector Extreme caution must be used to ensure that the sample does not concentrate too low or to dryness

8 Concentrate the extracts to <0 5ml on the N Evap under a gentle stream of nitrogen with the temperature not exceeding 35 C Extreme caution must be used to ensure that the sample does not concentrate too low or to dryness

9 Bring extract to 0 5ml F V in DCM Place in a labeled clear 2ml autosampler vial

10 Do FID screening (see CAS SOP)

11 Complete all necessary paperwork and benchsheet review checklist. Turn extracts and paperwork over to MS analysts

** following the above produces a calculated final volume of 5 0 ml**

UNCONTROLLED COPY

Test	Amount	Surrogate #1/ amount	Surrogate #2/ amount	Spike #1/ amount	Spike #2/ amount	cleanup	color	calculated final volume
8270 / 625	1 00 gram	Supelco 8-61376/ 50µl	Supelco 8-61377/ 100µl	Supelco 8-61378/ 500µl	Supelco 20198962/ 500µl	GPC	clear	5 ml.
8270-LL	1 00 gram	AP/125µl	n/a	8270/125µl	n/a	GPC	amber	5 ml.
SIM PAH / SIM-ALKH	1 00 gram	AP/50µl	n/a	PAH/500µl	n/a	Silica Gel*	green	5 ml
SIM PHEN	1 00 gram	AP/125µl	n/a	8270/250µl	n/a	GPC	red	5 ml
MISC								

** If carbazole is in the compound list do not silica gel do GPC*

STANDARD OPERATING PROCEDURE

SULFURIC ACID CLEANUP

EXT-3665

Revision 2

April 30 2007

UNCONTROLLED

Approved by _____ Supervisor _____ Date 5/1/07

_____ QA Manager _____ Date 5-1-07

_____ Laboratory Manager _____ Date 5/1/07

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2007

Annual review of this SOP has been performed and the SOP still reflects current practice
Initials _____ Date _____
Initials _____ Date _____
Initials _____ Date _____

DOCUMENT CONTROL
NUMBER _____
Initials _____ Date _____

SULFURIC ACID CLEANUP

1 SCOPE AND APPLICATION

1 1 This procedure is used to perform cleanup of sample extracts prior to analysis for polychlorinated biphenyls (PCBs), using EPA Method 3665A This procedure may be used when a sample matrix giving a complex chromatogram prevents accurate quantitation of PCBs The cleanup is applicable to extracts from all sample matrices This procedure should not be applied to cleanup of extracts for other target analytes as it will destroy most organic chemicals including the most organochlorine pesticides

UNCONTROLLED

1 2 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method

2 SUMMARY OF METHOD

The extract (in hexane) is sequentially treated with portions of concentrated sulfuric acid Appropriate caution must be taken when using concentrated sulfuric acid Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them If not in hexane already, it is important that all the extracts be exchanged to hexane before initiating the following treatments

COPY

3 INTERFERENCES

This technique will not destroy chlorinated benzenes, chlorinated naphthalenes (Halowaxes), and some chlorinated pesticides Care must be taken when interpreting chromatograms where these components may be present

4 SAFETY

4 1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined, however each chemical compound should be treated as a potential health hazard Exposure to these compounds should be reduced to the lowest possible level A reference file of material safety data sheets is available to all personnel involved in these analyses CAS also maintains a file of OSHA regulations regarding the safe handling of the chemicals specified in this method

4 2 Sample extracts and reagents should be handled in accordance with CAS safety policies An acid-proof apron gloves, and eye protection must be worn Also, see the **CAUTIONs** included for some steps

5 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the determinative method or SOP

6 REAGENTS

6 1 Pesticide grade solvents should be used in all steps of the procedure Other grades may be used, provided it is shown that the reagent is of sufficient purity to permit its use without adversely impacting the accuracy of the determination

6 2 Concentrated Sulfuric acid

UNCONTROLLED

6 3 Hexane, C_6H_{14} - Pesticide grade or equivalent

7 APPARATUS

7 1 Syringes, Pastuer pipets, or Class A volumetric pipets, 1 0 2 0 and 5 0 mL sizes

7 2 Vials - 1, 2 and 10 mL, glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops

7 3 Vortex mixer

COPY

8 RESPONSIBILITIES

8 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

8 2 It is the responsibility or the department supervisor/manager to document analyst training Documenting method proficiency, as described in the determinative method is also the responsibility of the department supervisor/manager

9 PROCEDURE

9 1 After the extract is brought to the desired final volume, transfer 1 0 or 2 0 mL of the hexane extract to a 10 mL vial and carefully add an equivalent volume of concentrated sulfuric acid This should be carried out in a fume hood The volume of hexane extract used depends on the requirements of the GC autosampler used for the analysis

CAUTION Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding

9 2 Cap the vial tightly and vortex for one minute A vortex must be visible in the vial

CAUTION Stop the vortexing immediately if the vial leaks AVOID SKIN CONTACT SULFURIC ACID BURNS

9 3 Allow the phases to separate for at least 1 minute All extracts should be centrifuged a minimum of 1 minute to separate phases, and centrifuged longer to if an emulsion exists Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

UNCONTROLLED

9 3 1 If a clean phase separation is achieved, proceed to Sec. 9.4.

9 3 2 If the hexane layer is colored or the emulsion persists after the first acid cleanup transfer the extract and let sit on 0 5g Florisil overnight Dispose of the acid layer properly

9 4 Transfer the hexane layer to a clean 2 mL autosampler vial and cap Take care not to include any of the acid layer in this clean vial, as it can cause damage to the instrumentation

COPY

10 QUALITY CONTROL

Refer to the determinative method or SOP

11 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly

12 WASTE MANAGEMENT

The laboratory will comply with all Federal, State, and local regulations governing waste management particularly the hazardous waste identification rules and land disposal restrictions as specified in the laboratory Safety Manual, Sections 6 and 7

13 REFERENCES

U S EPA Test Methods for Evaluating Solid Waste, SW-846 Update II September 1994
Method 3665, Revision 0

U S EPA Test Methods for Evaluating Solid Waste SW-846 Update III, December 1996
Method 3665A, Revision 1

UNCONTROLLED

COPY

STANDARD OPERATING PROCEDURE

SPECIFIC GRAVITY

GEN-SPECGRAV

UNCONTROLLED

Revision 0
June 6 2005

Approved By _____ Supervisor 6/6/05 Date

_____ QA Manager 6-6-05 Date

_____ Laboratory Manager 6/6/05 Date

COPY

COLUMBIA ANALYTICAL SERVICES, INC
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc 2005

Annual review of this SOP has been performed and the SOP still reflects current practice	
Initials ___	Date 8/9/06
Initials ___	Date ___
Initials ___	Date ___

DOCUMENT CONTROL	
NUMBER ___	
Initials ___	Date ___

SPECIFIC GRAVITY

1 SCOPE AND APPLICATION

1 1 This Standard Operating Procedure (SOP) is used to determine the specific gravity of liquids, aqueous sludge, non-aqueous sludge, and solid material (including sediment and soil) The nature of the sample will usually determine which method is to be followed

UNCONTROLLED

1 2 The two methods used in this SOP are Standard Methods method 2710F for liquid and aqueous sludge, and ASTM D854-83 for non-aqueous sludge and solid material.

2 METHOD SUMMARY

In both methods the specific gravity is determined by comparing the mass of a known volume of homogeneous sample at a specific temperature to the mass of the same volume of de-ionized water

3 DEFINITIONS

COPY

Specific Gravity The ration of the mass of a unit volume of a material at a stated temperature to the mass in air of the same volume of gas-free de-ionized water at a stated temperature

4 INTERFERENCES

There are no interferences associated with these methods, however large particles present in the sample will require a much larger container and a larger volume of sample to be used

5 SAFETY

All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves

Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method

6 SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

Liquid and aqueous sludge can be collected in either plastic bottles or glass jars Non-aqueous sludge and solids should be collected in glass jars

7 APPARATUS AND EQUIPMENT

7 1 Container A beaker or vial that can be marked and hold the known sludge volume during weighing

7 2 Pycnometer

UNCONTROLLED

7 3 Analytical Balance 0 1mg accuracy Alternately, for larger sample size up to 2 Kg capacity

7 4 Volumetric pipette 10 mL or 20 mL

8 STANDARDS, REAGENTS AND CONSUMABLE MATERIALS

De-ionized water

9 PREVENTATIVE MAINTENANCE

COPY

Thoroughly clean the pycnometer or beaker after each use

10 RESPONSIBILITIES

10 1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP This demonstration is in accordance with the training program of the laboratory Final review and sign-off of the data is performed by the department supervisor/manager or designee

10 2 It is the responsibility of the department supervisor/manager to document analyst training Documenting method proficiency as described in the *SOP for Documentation of Technical Personnel Training* is also the responsibility of the department supervisor/manager

11 PROCEDURE

11 1 SM 2710 F (Liquid and Aqueous Sludge)

11 1 1 Allow samples and an aliquot of de-ionized water to warm to room temperature

11 1 2 Tare a 20 mL scintillation vial and volumetrically pipette 10 mL de-ionized water Record the weight W

11 1 3 Mark the vial at the bottom of the meniscus of the water

11 1 4 Empty and dry the vial

11 1 5 Tare the vial and add homogenized sample to the mark and record the weight, S

11 1 6 Calculate the specific gravity, G, and report to three significant figures using the following equation $G = S / W$

UNCONTROLLED

11.2 ASTM D854-83 (Non-aqueous Sludge, Soils, Sediments and other Solids)

11 2 1 It is intended that the following procedure be used for samples passing a No 4 (4 75mm) sieve For particle sizes larger than a No, 4 sieve, refer to GEN-E1109 SOP, Bulk Density of Solid Waste Fractions

11 2 2 Allow samples and an Aliquot of de-ionized water to warm to room temperature

11 2 3 Record the tare weight of the clean, dry pycnometer with the stoppered thermometer inserted into the opening and the glass cover on the vent hole

COPY

11 2 4 Fill the pycnometer to about half way up the neck with de-ionized water Insert the stoppered thermometer into the neck slowly allowing all air and excess water to escape through the neck and the vent hole Dry the outside of the pycnmoeter and place the glass cover over the vent hole Record the weight of the water, Wa

11 2 5 Empty the water out of the pycnometer and tare on the balance Add approximately 2 0 g of homogenized sample to the pycnometer and record the weight of the wet sample, Wo

11 2 6 Add deionized water to about halfway up the neck of the pycnometer Insert the stoppered thermometer into the neck slowly allowing all air and excess water to escape through the neck and the vent hole Dry the outside of the pycnmoeter and place the glass cover over the vent hole Tare the balance and record the weight of the pycnometer sample, and water Subtract the tare weight of the pycnometer and record the weight of the sample and water, Wb

11 2 7 Record the temperature of the sample and water

11 2 8 Calculate the Specific Gravity, G, and report to three significant figures using the following equation

$$G = \frac{Wo}{[Wo + (Wa-Wb)]}$$

12 QUALITY CONTROL

12 1 All quality control data should be maintained and available for easy reference or inspection

12.2 Run one duplicate sample for every sample batch of 20 or per Service Request tier II or higher, whichever is more frequent

UNCONTROLLED

12.3 The Relative Percent Difference (RPD) between duplicate sample analyses must be ≤ 20

13 DATA REDUCTION, REVIEW, AND REPORTING

13 1 The data packet for the sequence is submitted for review by the supervisor or designee The results are transferred to the appropriate report form located in the CAS network directory R \WET\WIP These forms are made from templates located in R \WET\FORMS Once the results are transferred, the report is reviewed

COPY

13 2 Refer to the SOP for Laboratory Data Review Process for instructions for data review

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s) Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements

15 METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision Refer to the reference method for additional method performance data available

16 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible Standards are prepared in volumes consistent with

methodology and only the amount needed for routine laboratory use is kept on site The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly

17 WASTE MANAGEMENT

The laboratory will comply with all Federal State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual

18 REFERENCES

18.1 Standard Methods Method 2710 F, Standard Methods for the Examination of Water and Wastewater, 20th Ed , 1998

18 2 ASTM Method D854, November 1983

UNCONTROLLED

COPY

APPENDIX A

UNCONTROLLED

COPY

Columbia Analytical Services Inc

Service Request # _____ Method SM2710 F

Analysis For Specific Gravity / Bulk Density

Sample	Weight of 10ml Sample	Specific Gravity

UNCONTROLLED COPY

Comments **Weight of 10 ml DI water =** _____

Analyzed By	Date
Reviewed By	Date

SPECGRAV XLS

Columbia Analytical Services Inc

Service Request # _____ Method ASTM D 854 83

Analysis For Specific Gravity Matrix Soil / Solid

Sample Number	Tare	Wet Weight (Wo)	Water Weight (Wa)	Sample Weight (Wb)	T (C)	Specific Gravity

UNCONTROLLED COPY

Calculation $\frac{Wo}{[Wo + (Wa-Wb)]}$

Wo = **Wet Weight (Sample)**
Wa = **Water Weight**
Wb = **Sample + Water Weight**

Comments _____

Analyzed By	Date
Reviewed By	Date

SPGRAV XLT

1 0 SCOPE

1 1 This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from solid waste matrices soils sediments and ground water It is based on the EPA s SWA-846 method 8270C and the Puget Sound Estuary Protocol (marine sediments) Direct injection of a sample may be used in limited applications The method is normally used to determine the compounds in Table 1 Additional compounds that are less frequently determined are listed in Table 2

1 2 The following compounds may require special treatment when being determined by this method Benzidine can be subject to oxidative losses during solvent concentration Also, chromatography is poor Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph chemical reaction in acetone solution and photochemical decomposition N nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenyl amine Pentachlorophenol 2 4-dinitrophenol, 4 nitrophenol 4 6-dinitro-2-methylphenol 4-chloro-3-methylphenol benzoic acid 2-nitroaniline, 3-nitroaniline 4-chloroaniline and benzyl alcohol are subject to erratic chromatographic behavior especially if the GC system is contaminated with high boiling material

1 3 The practical quantitation limit (PQL) of this method for determining an individual compound is approximately 330 µg/kg (wet weight) for soil/sediment samples and 10 µg/L for ground water samples (see Table 5 for PQLs) PQLs will be higher depending upon dilution required and the moisture content of the sample

1 4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra Each analyst must demonstrate the ability to generate acceptable results with this method

2 0 SUMMARY OF METHOD

Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods This method describes chromatographic conditions that will allow for the separation of the compounds in the extract

2 1 Water samples will be prepared utilizing continuous liquid/liquid extraction AC G-3520

2 2 Soil samples will be prepared utilizing ultrasonic extraction AC G-3550

2 3 Sediment samples will be prepared utilizing ultrasonic extraction AC G-3550 or soxhlet extraction AC G-3540 Sediment samples may require larger sample sizes and a modified calibration curve to achieve the required detection limits Marine Sediment PSEP sample preparation method modifications are detailed in Appendix 3

2 4 All soil and sediment samples will be cleaned up by gel permeation chromatography AC G-3640-GPC

2 5 Sediment samples may require a silica gel clean-up procedure AC G-3630 if the analysis is for polyaromatic hydrocarbons only

3 0 INTERFERENCES

3 1 Raw GC/MS data from all blanks samples and spikes must be evaluated for chromatographic interferences caused by the preparative steps performed prior to analysis or instrumental procedures Common sources of interferences include solvents, reagents and GPC carry-over from contaminated samples

3 2 Contamination by GC carryover can occur whenever high level and low level samples are sequentially analyzed To reduce carryover the sample syringe must be rinsed out between samples with solvent Whenever an unusually concentrated sample is encountered it should be followed by the analysis of solvent to check for cross contamination

4 0 ESTIMATE OF ANALYTICAL TIME

4 1 Tuning and initial calibration require approximately 6 hours of instrument time prior to analysis of samples If a valid calibration is available approximately 2 hours is required for tuning and calibration verification

4 2 Sample analysis requires approximately 1 hour of instrument time per sample Data work up and reporting varies depending on sample type and reporting requirements 1 to 2 hours should be anticipated per sample

5 0 AMOUNT OF SAMPLE

5 1 Water samples require 1 liter of sample An additional liter is required for each duplicate matrix-spike or matrix-spike duplicate

5 2 Soil samples require approximately 50 grams for sample extraction pH determination and moisture determination An additional 30 grams is required for each duplicate matrix spike or matrix spike duplicate

5 3 Sediment samples require the same amount of sample as soils unless low detection limits are required such as for Puget Sound Protocol Marine Sediment PSEP sample amount requirements are detailed in Appendix 3

6 0 SAMPLE EXTRACT HANDLING AND STORAGE

6 1 Store sample extracts at 4°C until analysis

6 2 Store sample extracts for 365 days following analysis at -10° to -20° C

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

6 3 Analyze sample extracts within 35 days

7 0 APPARATUS AND MATERIALS

7 1 Gas chromatograph/mass spectrometer system – Hewlitt Packard 5972 MSD, capable of scanning from 35 to 500 amu every 1 sec using 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 1µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP)

7 2 Gas chromatograph - Hewlett Packard 5890 Series II with Hewlett Packard 5973A autosampler equipped with Split/Splitless injector

7 3 Syringe - Hamilton 701ASN 10µL

7 4 Column - 30 m x 0 25 mm i d 0 25-µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5MS is preferred but equivalent columns are acceptable)

7 5 Data system - Data analysis performed using Chemserver software on a HP/UX J5600 computer Final data reports are generated in US-EPA CLP format (OLM 3 0) using Thruput Target and Envision software

8 0 REAGENTS

8 1 All solvents used will be pesticide-residue grade or better

8 2 Standard solutions - Standard solutions are purchased as certified solutions

8 2 1 Commercially certified stock standards are used with the exception of alpha-terpineol See standards preparation AC G-ORGSTD for standard preparation procedures If the compound purity is assayed to be 96% or greater when stock solutions are prepared the mass may be used without correction to calculate the concentration of the stock standard

8 2 2 Secondary standard solutions will be stored at 4°C and protected from light Stock standard solutions will be stored at -10° to -20°C and protected from light All standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards or samples from them The level of the solution in the container should be marked after each use so any evaporation can be detected

8 2 3 The stock standard solutions must be replaced according to the manufactures expiration date Working standards are replaced after 1 year or at the stocks expiration date (whichever is less) or sooner if comparison with quality control check-samples indicates a problem

8 2 4 Internal standard solutions - The internal standards used are listed in Table 3 The internal standard spiking solution will contain each standard at a concentration of

2 000 ng/µL Each sample extract undergoing analysis should be spiked with 1 µL of the internal standard solution per 100 µL of sample extract, resulting in a concentration of 20 ng/µL of each internal standard with a 1000-µL final extract volume

8 2 5 GC/MS tuning standard consists of a methylene chloride solution containing 25 ng/µL of decafluorotriphenylphosphine (DFTPP)

8 2 6 Calibration standards

a A minimum of five calibration standards should be prepared

b The normal concentrations of the calibration standards will be 10 µg/mL 25 µg/mL 40 µg/mL 60 µg/mL and 80 µg/mL If decreased detection limits are required the additional calibration standards may be prepared down to a minimum concentration of 1 µg/mL

c Each standard contains each analyte for detection by this method (e g all of the compounds listed in Table 1 will be included) Compounds in Table 2 and selected additional compounds may be included if method performance criteria can be met

d Each aliquot of calibration standard is spiked with 1 µL of the internal standard solution per 100 µL of solution prior to analysis

8 2 7 Surrogate standards - The six surrogate compounds used are listed in Table 3 2-Chlorophenol-d4 and 1 2-Dichlorobenzene-d4 are also listed and may be used as alternate surrogate standards The acid surrogates (phenolic) are spiked to achieve a final concentration of 75 µg/mL The base/neutral surrogates are spiked to achieve a final concentration of 50 µg/mL The extraction procedures provide instruction for preparing and adding surrogate spikes

8 2 8 Laboratory control spike compounds (LCS) and matrix spike compounds are listed in Table 11 Full-target compound laboratory control spikes (FLCS) and matrix spike compounds are listed in Table 1 (Due to the cost involved FLCS are not analyzed unless requested by the client) Extraction procedures provide instruction for preparing and adding spike solutions

9 0 PROCEDURE

See Section 2 Summary of Method, for appropriate extraction methods

9 1 GC/MS operating conditions

9 1 1 Mass range 35-500 amu

9 1 2 Scan time 0 9 sec/scan 0 1 sec interscan time

9 1 3 Initial column temperature and hold time 40° C for 1 minute

Note If N nitrosodimethylamine is to be determined, the initial temperature must be reduced to 35° C and the initial hold time must be extended to approximately 5 minutes

9 1 4 Column temperature program 40-320° C at 8° C/min

9 1 5 Final column temperature hold 1-3 minutes @ 320° C

9 1 6 Injector temperature 270° C

9 1 7 Transfer line temperature 250° C

9 1 8 Source temperature 180° C

9 1 9 Injector Grob-type splitless

9 1 10 Sample volume 1 µL

9 1 11 Carrier gas Helium at 30 cm/sec

9 2 Instrument Tune - GC/MS system must be hardware-tuned to meet the criteria in Table 5 for a 50-ng injection of DFTPP Analyses may not begin for any standards or samples until all these criteria are met Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions It is suggested that the spectra for DFTPP be generated using a scan range ± 1 scan number from the scan number closest the total ion current maximum for DFTPP Mass spectrometer conditions must be identical for subsequent analysis of standards, samples QC samples and blanks associated with the DFTPP analysis

9 3 Injector and Column maintenance

9 3 1 The injector sleeve should be clean and compound breakdown or adsorption should be minimized

9 3 2 The capillary column should be in good condition with minimal tailing noted for reactive compounds such as pentachlorophenol

9 4 The internal standards should permit most of the components of interest in a chromatogram to have retention times of 0 80-1 20 relative to one of the internal standards Use the internal standards specified in Table 3 to calculate compound concentrations

9 5 Initial Calibration

9 5 1 Tune instrument as outlined in Section 9 2 above

9 5 2 Analyze 1 µL of five or more calibration standards (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1) Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes

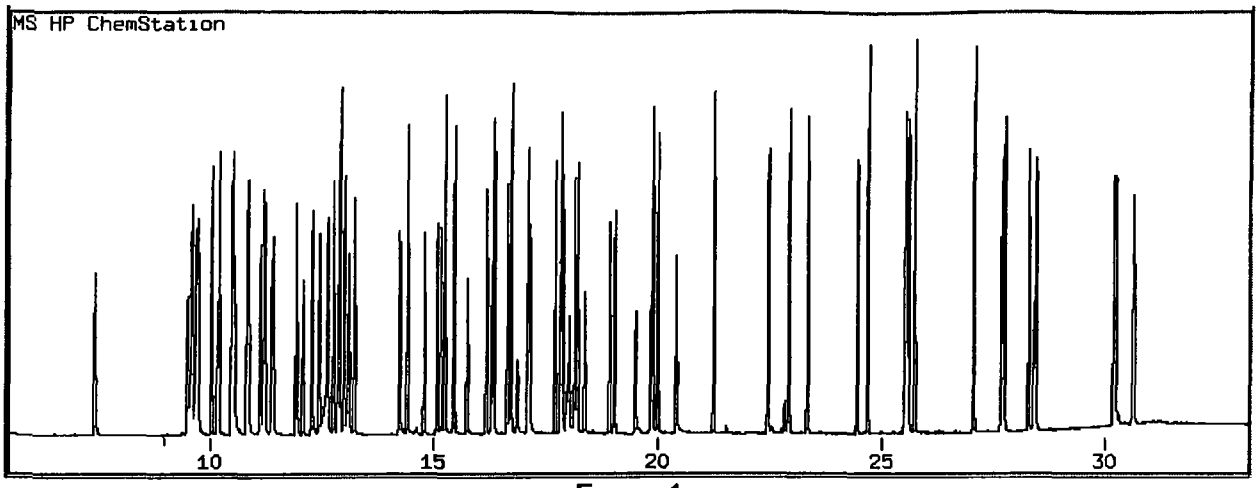


Figure 1

9 5 3 Calculate response factors (RFs) for each compound as shown below

RF = (AxCis)/(AisCx)

where

Ax = Area of the characteristic ion for the compound being measured

Ais = Area of the characteristic ion for the specific internal standard

Cx = Concentration of the compound being measured (µg/µL)

Cis = Concentration of the specific internal standard (µg/µL)

9 5 4

a Calculate the average RF and the percent relative standard deviation for each compound If the RSD of any target compound is 15 % or less the average relative response factor may be used for quantitation If the RSD is greater than 15 % Option 1 must be used

Option 1 – Calculate a linear calibration using least-squares regression for each compound exceeding the 15 % RSD criteria The correlation coefficient r must be greater than or equal to 0 99

If the correlation coefficient r is less than 0 99 Option 2 must be used

Option 2 – Calculate a non linear calibration using a quadratic- or third-order polynominal regression for each compound exceding the 15 % RSD criteria The coefficient of the determination COD must be greater than or equal to 0 99
Note SW-846 requires six calibration standards for second-order polynominals and seven calibration standards for third-order polynominals

If the coefficient of the determination COD is less than 0 99 Option 3 must be used

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Option 3 - Calculate the mean of the RSD values for all analytes in the calibration If it is less than or equal to 15% the initial calibration is valid Note A summary report indicating compounds that exceeded the 15% RSD criteria and the results of the mean RSD calculation is required

b The %RSD for each individual Calibration Check Compound (CCC) (see Table 6) must be less than 30% The relative retention times of each compound in each calibration run should agree within 0 06 relative retention time units If the CCCs are not included in the project compound list all compounds must meet the 30% RSD criteria

9 5 5 A system-performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used For semivolatiles the System Performance Check Compounds (SPCCS) are N-nitroso-di-n-propylamine hexachlorocyclo-pentadiene 2 4-dinitro-phenol and 4-nitrophenol The minimum acceptable average RF for these compounds is 0 050 These SPCCs typically have very low RFs (0 1-0 2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate They are usually the first to show poor performance Therefore they must meet the minimum requirement when the system is calibrated

9 6 Daily GC/MS calibration

9 6 1 Prior to analysis of the daily calibration check the GC/MS tuning standard must be analyzed and meet performance criteria as in 9 2

9 6 2 A 50-µg/mL calibration standard containing each compound of interest including all required surrogates must be performed every 12 hours immediately following DFTPP during analysis Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC and CCC criteria in 9 6 3 and 9 6 4

9 6 3 System Performance Check Compounds (SPCCs) A system performance check must be made during every 12-hour shift If the SPCC criteria are met a comparison of response factors is made for all compounds This is the same check that is applied during the initial calibration If the minimum response factors are not met the system must be evaluated and corrective action must be taken before sample analysis begins The minimum RF for semivolatile SPCCs is 0 050 Some possible problems are standard mixture degradation injection port inlet contamination contamination at the front end of the analytical column and active sites in the column or chromatographic system This check must be met before analysis begins

9 6 4 Calibration Check Compounds (CCCs) After the system performance check is met CCCs listed in Table 6 are used to check the validity of the initial calibration For compounds using an average response factor calculate the percent difference using

$$\%\,\text{Difference} = \frac{(RF_I - RF_C)}{\overline{RF_I}} \times 100$$

where

$\overline{RF_I}$ = average response factor from initial calibration

RF_c = response factor from current verification check standard

For compounds using a linear or non-linear calibration curve calculate the percent drift using

$$\%\,\text{Drift} = \frac{(\textit{Calculated concentration} \quad \textit{Theoretical concentration})}{\textit{Theoretical concentration}} \times 100$$

Where the calculated concentration is determined using the mean calibration factor

If the percent difference for each CCC is less than 20% the initial calibration is assumed to be valid If the criterion is not met (> 20% difference for any one CCC) corrective action must be taken If the CCCs are not included in the project compound list all compounds must meet the 20% RSD criteria Problems similar to those listed under SPCCs could affect this criterion If no source of the problem can be determined after corrective action has been taken a new five-point calibration must be generated This criterion must be met before sample analysis begins

9 6 5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition If the retention time for any internal standard changes by more than 30 seconds from the last daily calibration check, the chromatographic system must be inspected for malfunctions and corrections must be made as required If the Extracted Ion Current Profile (EICP) area for any of the internal standards changes by a factor of two (-50% to +100%) from the most recent initial calibration midpoint standard the mass spectrometer must be inspected for malfunctions and appropriate corrections must be made

9 7 GC/MS analysis

9 7 1 The extract may be screened on a GC/FID or GC/PID using the same type of capillary column This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds

9 7 2 Spike the sample extract or an aliquot of the sample extract with 1 µL of the internal standard solution (8 2 4) per 100 µL of sample extract just prior to analysis

9 7 3 Analyze the sample extract by GC/MS using the same conditions as were used for the initial and continuing calibration

9 7 4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system extract dilution must take place Additional internal standard must be added to the diluted extract to maintain the required 20 ng/µL of each internal standard in the extracted volume The diluted extract must be re-analyzed

9 7 5 After analysis store the extracts at 4° C, protected from light in vials equipped with unpierced Teflon lined septa

9 8 Data interpretation

9 8 1 Qualitative analysis

a An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum) Mass spectra for standard reference should be obtained on the GC/MS using the same operating conditions and DFTPP tune conditions as are used for sample analysis These standard reference spectra may be obtained through analysis of the calibration standards Two criteria must be satisfied to verify identification (1) elution of sample component at the same GC relative retention time (RRT) as the standard component, and (2) correspondence of the sample component and the standard component mass spectrum

b The sample component RRT must compare within ± 0 06 RRT units of the RRT of the standard component For reference, the standard must be run within the same 12 hours as the sample The RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest

c All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum

d The relative intensities of ions specified should agree within ± 20% between the standard and sample spectra

e If these criteria are not met but in the opinion of the mass spectral specialist the analyte is detected in the sample the analyte will be reported

f For samples containing components not associated with the calibration standards a library search may be made for the purpose of tentative identification The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other Only after visual comparison of sample spectra with the nearest library searches will the mass spectral specialist assign a tentative identification Guidelines for making tentative identification are

i Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum

ii The relative intensities of the major ions should agree within ± 20% (Example For an ion with an abundance of 50% in the standard spectrum the corresponding sample ion abundance must be between 30 and 70%)

iii Molecular ions present in the reference spectrum should be present in the sample spectrum

viii Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

v Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks Data system library reduction programs can sometimes create these discrepancies

9 8 2 Quantitative analysis

a When a compound has been identified the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion Quantitation will take place using the internal standard technique The internal standards to be used for each compound are listed in Table 7 If the compound does not appear in Table 7 the internal standard with a retention time nearest the retention time of that of a given analyte should be used

b Calculate the concentration of each identified analyte in the sample as follows

Water

$$\text{Concentration}(\mu g/L) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF})(V_o)(V_i)}$$

where

A_X = Area of characteristic ion for the compound being measured

I_s = Amount of internal standard injected (ng)

V_t = Volume of total extract taking into account dilutions (i e a 1 into 10 dilution of a 1-mL extract will mean Vt = 10 000 µL If half the base/neutral extract and half the acid extract are combined Vt = 2 000)

A_{is} = Area of characteristic ion for the internal standard

$\overline{RF}$ = Average Response factor for compound being measured (See IX F 4)

V_o = Volume of water extracted (mL)

V_i = Volume of extract injected (µL)

Sediment/Soil Sludge (dry-weight basis)

$$\text{Concentration}(\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF})(V_i)(W_s)(D)}$$

where

A_X, I_s V_t A_{is} $\overline{RF}$ V_i Are the same as for water

W_S = Mass of sample extracted or diluted in grams

D = (100 - % moisture)/100 or 1 for a wet-weight (as-received) basis

c Where applicable an estimate of concentration for non-calibrated components in the sample (tentatively identified compounds) should be made The formulas given above should be used with the following modifications The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1 The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration Use the nearest internal standard free of interferences

d Report results without correction for recovery data When duplicates and spiked samples are analyzed report all data obtained with the sample results

e Report results less than 10 parts-per-billion (PPB) to one significant figure Report results greater than 10 PPB to two significant figures

10 0 QUALITY CONTROL

10 1 Each day that an analysis is performed DFTPP tune standard and the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly Questions that should be asked are

10 1 1 Does the air leak spectrum look ok? Is there evidence of an injector/septum leak?

10 1 2 Does FC43 calibration gas look normal? Are the ratios of m/z's 69 131 219 and 502 correct? Does the resolution look normal?

10 1 3 Does DFTPP meet criteria in Table 5 easily?

10 1 4 Do the chromatograhic peaks look normal for DFTPP and for the daily calibration standard?

10 1 5 Is the response obtained comparable to the response from previous DFTPP analyses and daily calibration analyses?

If any of the above do not appear normal make appropriate corrections before attempting to analyze samples

10 2 Required instrument QC before samples may be analyzed

10 2 1 The GC/MS system must be tuned to meet the DFTPP specifications in Table 5

10 2 2 Before processing any samples, the analyst should demonstrate, through the analysis of the method blank associated with the samples that interferences from the analytical system and sample extraction are under control Each set of samples that is extracted will be extracted with a method blank The blanks must be carried through all stages of sample preparation and measurement with the samples

10 2 3 There must be an initial calibration of the GC/MS system as specified in 9 5

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

10 2 4 The GC/MS system must meet the SPCC criteria specified in 9 6 3 and the CCC criteria in 9 6 4 each 12-hour period

10 3 To establish the ability to generate acceptable accuracy and precision the analyst must perform an initial demonstration of precision and accuracy (IPAR) as outlined in SOP OQ-TRAIN

10 3 1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 100 µg/mL in acetone The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions If prepared by the laboratory the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration

10 3 2 Using a gas tight syringe prepare QC reference samples at a concentration of 100 µg/L by adding 1 00 mL of QC reference sample concentrate to each of four 1-L aliquots of water

10 3 3 Analyze the well-mixed QC reference samples according to the method beginning in section 9 with extraction of the samples

10 3 4 Calculate the average recovery (x) in µg/L and the standard deviation (s) of the recovery in µg/L for each analyte of interest using the four results

10 3 5 For each analyte, compare s and x with the corresponding acceptance criteria for precision and accuracy respectively found in Table 9 If s and x for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin If any individual s exceeds the precision limit or any individual x falls outside the range for accuracy then the system performance is unacceptable for that analyte

NOTE The large number of analytes in Table 9 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed

10 3 6 When one or more of the analytes tested fail at least one of the acceptance criteria the analyst must locate and correct the source of the problem and repeat the test for all analytes of interest beginning with 9 6 Repeated failure may require recalibration beginning with 9 5

10 4 The laboratory must analyze a reagent blank for each analytical batch (up to a maximum of 20 samples/batch except for samples required under regulation which need QC every 10 samples) and should analyze a Laboratory Control Spike (LCS) for each analytical batch A matrix spike and matrix spike duplicate should be analyzed for each 20 samples, except for samples required under regulation Regulatory samples need QC every 10 samples Matrix spikes may not be analyzed with each extraction batch

Compare the percent recovery (p_s) for each analyte in the LCS with the laboratory generated QC charts (generated in 10 5 1a) If the recovery of any analytes of interest falls outside the designated range the laboratory performance for that analyte is judged to be out of control and the problem identified and corrected The analytical result for that analyte in the unspiked sample is suspect and if possible the samples associated with the LCS should be reanalyzed

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

10 5 As part of the QC program for the laboratory method accuracy and precision for each matrix studied must be assessed and records must be maintained

10 5 1 To determine acceptable accuracy and precision limits for LCS samples the following procedure should be performed

a After the analysis of five LCS (of the same matrix) calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p) Plot p with a percent recovery interval of p - 2 s_p to p + 2 s_p with s the control limit and p - 3 s_p to p + 3 s_p as the action limit (For example if p = 90% and s_p = 10% the control limit is 70-110% and the action limit is 60-120%) Update the recovery charts for each analyte on a regular basis (e g after each ten new measurements)

b Only the twenty most recent LCS should be used to generate the QC limits

c For aqueous and soil matrices, these laboratory established LCS action limits may if applicable be compared with the control limits listed in Table 11

10 5 2 To determine acceptable accuracy and precision limits for surrogate standards the following procedure will be performed

a After the analysis of five method blanks (of the same matrix) calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p) Plot p with a percent recovery interval of p - 2 s_p to p + 2 s_p as the control limit and p - 3 s_p to p + 3 s_p as the action limit (For example if p = 90% and s_p = 10% the control limit is 70-110% and the action limit is 60-120%) Update the recovery charts for each analyte on a regular basis (e g after each twenty new measurements)

b For aqueous matrices these laboratory established action limits should, if applicable be compared with the control limits listed in Table 10 The limits given are multi-laboratory performance based limits from EPA 8270 Rev 1 for soil and aqueous samples Therefore the single-laboratory limits established in the recovery chart must fall within those given in Table 10 for these matrices

c If recovery is not within limits, the following procedures are required Check to be sure there are no errors in calculations surrogate solutions and internal standards Also, check instrument performance Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem If possible re-extract and re-analyze the sample if none of the above are a problem or note the recovery problem in the report narrative

10 6 An MDL Study will be performed at least once per year as outlined in SOP AQ G-MDL

11 0 REFERENCES

11 1 U S EPA 40 CFR Part 136 'Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act Method 625 ' October 26 1984

11 2 U S EPA Contract Laboratory Program Statement of Work for Organic Analysis July 1985 Revision

11 3 Provost L P and R S Elder "Interpretation of Percent Recovery Data " American Laboratory 15 58-63 1983

11 4 Eichelberger J W L E Harris and W L Budde 'Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography Mass Spectrometry Systems " Analytical Chemistry 47 995-1000 1975

11 5 "Method Detection Limit for Methods 624 and 625 " Olynyk P W L Budde and J W Eichelberger Unpublished report October 1980

11 6 "Interlaboratory Method Study for EPA Method 625-Base/Neutrals Acids and Pesticides " Final Report for EPA Contract 68-03-3102 (in preparation)

11 7 Burke J A 'Gas Chromatography for Pesticide Residue Analysis Some Practical Aspects ' Journal of the Association of Official Analytical Chemists 48 1037 1965

11 8 Lucas S V Kornfeld, R A "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes " U S Environmental Protection Agency Environmental Monitoring and Support Laboratory Cincinnati OH 45268 February 20 1987 Contract No 68-03-3224

11 9 Engel T M , Kornfeld R A Warner J S Andrews K D 'Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846 Method 3510" U S Environmental Protection Agency Environmental Monitoring and Support Laboratory Cincinnati OH 45268 June 5 1987, Contract 68 03-3224

11 10 U S EPA Contract Laboratory Program Statement of Work for Organic Analysis OLM1 8

11 12 U S EPA Method 8270 Revision 1 December 1987

12 0 REVISION HISTORY

12 1 7/17/07 – Updated references to SOPs and made small corrections to directions regarding which section to which one should refer

12 2 6/19/09 – Updated reporting limits

Table 1 -- List of characteristic ions of semi-volatile compounds

Compound	CAS#	Primary Ion	Secondary Ions
Acenaphthene	83-32-9	154	153 152
Acenaphthylene	208-96-8	152	151, 153
Anthracene	120-12-7	178	176, 179
Benz(a)anthracene	56-55-3	228	229, 226
Benzo(b)fluoranthene	205-99-2	252	253 125
Benzo(k)fluoranthene	207-08-9	252	253 125
Benzo(g h,i)perylene	191-24-2	276	138 277
Benzo(a)pyrene	50-32-8	252	253, 125
Bis(2-chloroethoxy)methane	111-91-1	93	95, 123
Bi-s(2-chloroethyl)ether	111-44-4	93	63, 95
Bis(2-chloroisopropyl)ether	39638-32-9	45	77, 121
Bis(2-ethylhexyl)phthalate	117-81-7	149	167 279
4-Bromophenyl phenyl ether	101-55-3	248	250 141
Butyl benzyl phthalate	85-68-7	149	91, 206
4-Chloroaniline	106-47-8	127	129
4-Chloro-3 methylphenol	59-50-7	107	144, 142
2-Chloronaphthalene	91-58-7	162	127 164
2-Chlorophenol	95-57-8	128	64 130
4-Chlorophehyl phenyl ether	7005-72-3	204	206 141
Chrysene	218-01-9	228	226, 229
Dibenz(a h)anthracene	53-70-3	278	139, 279
Dibenzofuran	132-64-9	168	139
Di-n-butylphthalate	84-74-2	149	150, 104
1,2-Dichlorobenzene	95-50-1	146	148 111
1 3-Dichlorobenzene	541-73-1	146	148, 111
1,4-Dichlorobenzene	106-46-7	146	148, 111
3 3-Dichlorobenzidine	91-94-1	252	254, 126
2,4-Dichlorophenol	120-83-2	162	164, 98
Diethyl phthalate	84 66-2	149	177 150
2,4-Dimethylphenol	105-67-9	122	107, 121
Dimethyl phthalate	131-11-3	163	194, 164
4,6-Dinitro-2-methylphenol	534-52-1	198	51, 105
2,4-Dinitrophenol	51-28-5	184	63, 154
2,4-Dinitrotoluene	121-14-2	165	63, 89
2,6-Dinitrotoluene	606-20-2	165	63, 89
1,2-Diphenylhydrazine	122-66-7	77	105, 182
Di-n-octylphthalate	117-84-0	149	167, 43
Fluoranthene	206-44-0	202	101, 203
Fluorene	86-73-7	166	165, 167
Hexachlorobenzene	118-74-1	284	142, 149
Hexachlorobutadiene	87-68-3	225	223, 227
Hexachlorocyclopentadiene	77-47-4	237	235, 272
Hexachloroethane	67-72-1	117	201, 199
Indeno(1 2 3-cd)pyrene	193-39-5	276	138 227
Isophorone	78-59-1	82	95 138

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Compound	CAS#	Primary Ion	Secondary Ions
2-Methylnaphthalene	91-57-6	142	141
2-Methylphenol	95-48-7	108	107 79
4-Methylphenol	106-44-5	108	107 79
Naphthalene	91-20-3	128	129 127
2-Nitroaniline	88-74-4	65	92 138
3-Nitroaniline	99-09-2	138	108 92
4-Nitroaniline	100-01-6	138	108 92
Nitrobenzene	98-95-3	77	123 65
2-Nitrophenol	88-75-5	139	109, 65
4-Nitrophenol	100-02-7	139	109 65
N Nitrosodiphenylamine	86-30-6	169	168 167
N Nitrosodi-n-propylamine	621-64-7	70	42 101 130
Pentachlorophenol	87-86-5	266	264 268
Phenanthrene	85-01-8	178	179 176
Phenol	108-95-2	94	65 66
Pyrene	129-00-0	202	200 203
1 2 4-Trichlorobenzene	120-82-1	180	182 145
2 4 5-Trichlorophenol	95-95-4	196	198 200
2,4,6-Trichlorophenol	88-06-2	196	198 200

Table 2 – List of characteristic ions of semi-volatile compounds

Compound	CAS#	Primary Ion	Secondary Ions
Benzidine	92-87-5	184	92, 185
Benzoic acid	65-85-0	122	105, 77
Benzyl alcohol	100-51-6	108	79 77
N-Nitrosodimethylamine	62-75-9	42	74 44
3-Methylphenol	108-39-4	108	107 79
Pyridine	110-86-1		

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Table 3 - Internal Standards and Surrogates

Compound	Primary Ion	Secondary Ions
Internal Standards		
1 4-Dichlorobenzene-d4	152	115
Naphthalene-d8	136	68
Acenaphthene d10	164	162 160
Phenanthrene-d10	188	94, 80
Chrysene-d12	240	120, 236
Perylene-d12	264	260, 265
Surrogates		
Phenol-d5	99	42, 71
2-Fluorophenol	112	64
2,4 6-Tribromophenol	330	332, 141
Nitrobenzene-d5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122 212
2-Chlorophenol-d4(alternate)	132	68 134
1 2-Dichlorobenzene-d4(alternate)	152	115, 150

Table 4 - PQLs FOR SEMIVOLATILE ORGANICS[b]
(EPA METHOD 8270, 1987 Rev 1)

	Practical Quantitation Limits[b]	
Semivolatiles	Ground Water µg/L	Low Soil/ Sediment µg/kg
Acenapthene	10	330
Acenaphthylene	10	330
Anthracene	10	330
Benz(a)anthracene	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzoic acid	10	330
Benzo(g,h,i)perylene	10	330
Benzo(a)pyrene	10	330
Benzyl alcohol	10	330
Bis(2-chloroethoxy) methane	10	330
Bis(2-chloroethyl) ether	10	330
Bis(2-chloroisopropyl) ether	10	330
Bis(2-ethylhexyl)phthalate	10	330
4-Bromophenyl phenyl ether	10	330
Butyl benzyl phthalate	10	330
4-Chloroaniline	10	330
4-Chloro-3 methylphenol	10	330
2-Chloronaphthalene	10	330

Semivolatiles	Ground Water µg/L	Low Soil/ Sediment µg/kg
2-Chlorophenol	10	330
4-Chlorophenyl phenyl ether	10	330
Chrysene	10	330
Dibenz(a h)anthracene	10	330
Dibenzofuran	10	330
Di-n-butylphthalate	10	ND
1,2-Dichlorobenzene	10	330
1,3-Dichlorobenzene	10	330
1 4-Dichlorobenzene	10	330
3,3 -Dichlorobenzidine	10	330
2,4-Dichlorophenol	10	330
Diethylphthalate	10	330
2,4-Dimethylphenol	10	330
Dimethyl phthalate	10	330
4 6-Dinitro-2-methylphenol	10	330
2 4-Dinitrophenol	10	330
2 4-Dinitrotoluene	10	330
2 6-Dinitrotoluene	10	330
Di-n-octyl phthalate	10	330
Fluoranthene	10	330
Fluorene	10	330
Hexachlorobenzene	10	330
Hexachlorobutadiene	10	330
Hexachlorocyclopentadiene	10	330
Hexachloroethane	10	330
Indeno(1 2 3-cd)pyrene	10	330
Isophorone	10	330
2-Methylnaphthalene	10	330
2-Methylphenol	10	330
3-Methylphenol	10	ND
4-Methylphenol	10	330
Naphthalene	10	330
2-Nitroaniline	10	330
3-Nitroaniline	10	330
4-Nitroaniline	10	ND
Nitrobenzene	10	330
2-Nitrophenol	10	330
4-Nitrophenol	10	330
N-Nitrosodiphenylamine	10	330
N-Nitroso-di-n propylamine	10	330
Pentachlorophenol	10	330
Phenanthrene	10	330
Phenol	10	330
Pyrene	10	330
Pyridine	ND	ND

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Semivolatiles	Ground Water µg/L	Low Soil/ Sediment µg/kg
1 2 4-Trichlorobenzene	10	330
2,4,5-Trichlorophenol	10	330
2 4,6-Trichlorophenol	10	330

PQLs listed for soil/sediment are based on wet mass Normally data is reported on a dry-weight basis, therefore PQLs will be higher based on the % moisture in each sample based on a 30-g sample and gel permeation chromatography cleanup

b Sample PQLs are highly matrix-dependent The PQLs listed herein are provided for guidance and may not always be achievable
ND - Not determined
NA - Not applicable

Table 5 - DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

Table 6 - CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1 4-Dichlorobenzene	2 4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenyl ami-ne	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2 4 6-Trichlorophenol
Benzo(a)pyrene	

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Table 7 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaghthene-d10
Benzyl alcohol	Benzoic acid	Acenaphthene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	Acenaphthylene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3 methylphenol	4 Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2 4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1 2-Dichlorobenzene	2,4-Dimethylphenol	Dimethyl phthalate
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	Isophorone	2,4-Dinitrotoluene
2-Methylphenol	Naphthalene	2 6-Dinitrotoluene
4 Methylphenol	Nitrobenzene	Fluorene
N-Nitrosodimethylamine	Nitrobenzene-d8 (surr)	2-Fluorobiphenyl (surr)
N-Nitroso-di-n-propylamine	2-Nitrophenol	Hexachlorocyclopentadiene
Phenol	1,2,4-Trichlorobenzene	2-Nitroaniline
Phenol-d6 (surr)		3-Nitroaniline
		4-Nitroaniline
		4-Nitrophenol
		1 2,4,5-Tetrachlorobenzene
		2 4 6-Tribromophenol (surr)
		2 4 6-Trichlorophenol
		2,4 5-Trichlorophenol

Phenanthrene-d10	Chrysene-d12	Perylene-d12
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	3 3'-Dichlorobenzidine	Di-n-octylphthalate
Fluoranthene	Pyrene	Indeno(1 2 3-cd)pyrene
Hexachlorobenzene	Terphenyl-dl4 (surr)	
N-Nitrosodiphenylamine		
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Table 8 - QC ACCEPTANCE CRITERIAa
(EPA METHOD 8270C 1996 Rev 3)

Parameter	Test conc (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p, p_s (%)
Acenaphthene	100	27 6	60 1-132 3	47-145
Acenaphthylene	100	40 2	53 5-126 0	33-145
Anthracene	100	32 0	43 4-118 0	27 133
Benz(a)anthracene	100	27 6	41 8-133 0	33-143
Benzo(b)fluoranthene	100	38 8	42 0-140 4	24-159
Benzo(k)fluoranthene	100	32 3	25 2-145 7	11-162
Benzo(a)pyrene	100	39 0	31 7-148 0	17-163
Benzo(ghi)perylene	100	58 9	D-195 0	D-219
Benzyl butyl phthalate	100	23 4	D-139 9	D-152
Bis(2-chloroethyl)ether	100	55 0	42 9-126 0	12-158
Bis(2-chloroethoxy)methane	100	34 5	49 2-164 7	33-184
Bis(2-chloroisopropyl)ether	100	46 3	62 8-138 6	36-166
Bis(2-ethylhexyl)phthalate	100	41 1	28 9-136 8	8-158
4-Bromophenyl phenyl ether	100	23 0	64 9-114 4	53-127
2-Chloronaphthalene	100	13 0	64 5-113 5	60-118
4-Chlorophenyl phenyl ether	100	33 4	38 4-144 7	25-158
Chrysene	100	48 3	44 1-139 9	17-168
Dibenzo(a h)anthracene	100	70 0	D-199 7	D-227
Di-n-butyl phthalate	100	16 7	8 4-111 0	1-118
1,2-Dichlorobenzene	100	30 9	48 6-112 0	32-129
1,3-Dichlorobenzene	100	41 7	16 7-153 9	D-172
1 4-Dichlorobenzene	100	32 1	37 3-105 7	20-124
3,3'-Dichlorobenzidine	100	71 4	8 2-212 5	D-262
Diethyl phthalate	100	26 5	D 100 0	D-114
Dimethyl phthalate	100	23 2	D-100 0	D-112
2,4-Dinitrotoluene	100	21 8	47 5-126 9	39-139
2,6-Dinitrotoluene	100	29 6	68 1-136 7	50-158
Di-n-octylphthalate	100	31 4	18 6-131 8	4-146
Fluoranthene	100	32 8	42 9-121 3	26-137
Fluorene	100	20 7	71 6-108 4	59-121
Hexachlorobenzene	100	24 9	7 8-141 5	D-152
Hexachlorobutadiene	100	26 3	37 8-102 2	24-116
Hexachloroethane	100	24 5	55 2-100 0	40-113
Indeno(1,2 3 cd)pyrene	100	44 6	D-150 9	D-171
Isophorone	100	63 3	46 6-180 2	21-196
Naphthalene	100	30 1	35 6-119 6	21-133
Nitrobenzene	100	39 3	54 3-157 6	35-180
N-Nitrosodi-n-propylamine	100	55 4	13 6-197 9	D-230
Phenanthrene	100	20 6	65 2-108 7	54-120
Pyrene	100	25 2	69 6-100 0	52-115
1 2 4-Trichlorobenzene	100	28 1	57 3-129 2	44-142
4-Chloro-3-methylphenol	100	37 2	40 8-127 9	22-147

Parameter	Test conc (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p, p_s (%)
2-Chlorophenol	100	28 7	36 2-120 4	23-134
2 4-Chlorophenol	100	26 4	52 5-121 7	39-135
2 4-Dimethylphenol	100	26 1	41 8-109 0	32-119
2,4-Dinitrophenol	100	49 8	D-172 9	D-191
2-Methyl-4 6-dinitrophenol	100	93 2	53 0-100 0	D-181
2-Nitrophenol	100	35 2	45 0-166 7	29-182
4-Nitrophenol	100	47 2	13 0-106 5	D-132
Pentachlorophenol	100	48 9	38 1-151 8	14-176
Phenol	100	22 6	16 6-100 0	5-112
2 4 6-Trichlorophenol	100	31 7	52 4-129 2	37-144

s = Standard deviation of four recovery measurements in µg/L
x = Average recovery for four recovery measurements in µg/L
p p_s = Percent recovery measured
D = Detected result must be greater than zero

a criteria from 40 CFR Part 136 for Method 625 These criteria are based directly on the method performance data in Table 7 Where necessary the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Table 9 - ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION
(EPA METHOD 8270C 1996 Rev 3)

Parameter	Accuracy, as recovery, X (µg/L)	Single analyst precision, s_r (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0 96C+0 19	0 15x-0 12	0 21x-0 67
Acenaphthylene	0 89C+0 74	0 24x-1 06	0 26x-0 54
Anthracene	0 80C+0 68	0 21x-0 32	0 27x-0 64
Benz(a)anthracene	0 88C-0 60	0 15x+0 93	0 26x-0 21
Benzo(b)fluoranthene	0 93C-1 80	0 22x+0 43	0 29x+0 96
Benzo(k)fluoranthene	0 87C-1 56	0 19x+1 03	0 35x+0 40
Benzo(a)pyrene	0 90C-0 13	0 22x+0 48	0 32x+1 35
Benzo(ghi)perylene	0 98C-0 86	0 29x+2 40	0 51x-0 44
Benzyl butyl phthalate	0 66C-1 68	0 18x+0 94	0 53x+0 92
Bis(2-chloroethyl)ether	0 86C-1 54	0 35x-0 99	0 35x+0 10
Bis(2-chloroethoxy)methane	1 12C-5 04	0 16x+1 34	0 26x+2 01
Bis(2-chloroisopropyl)ether	1 03C-2 31	0 24x+0 28	0 25x+1 04
Bis(2-ethylhexyl)phthalate	0 84C-1 18	0 26x+0 73	0 36x+0 67
4-Bromophenyl phenyl ether	0 91C-1 34	0 13x+0 66	0 16x+0 66
2-Chloronaphthalene	0 89C+0 01	0 07x+0 52	0 13x+0 34
4-Chlorophenyl phenyl ether	0 91C+0 53	0 20x-0 94	0 30x-0 46
Chrysene	0 93C-1 00	0 28x+0 13	0 33x-0 09
Dibenzo(a,h)anthracene	0 88C+4 72	0 30x+8 51	0 59x+0 25
Di-n-butyl phthalate	0 59C+0 71	0 13x+1 16	0 39x+0 60
1 2-Dichlorobenzene	0 80C+0 28	0 20x+0 47	0 24x+0 39
1 3-Dichlorobenzene	0 86C-0 70	0 25x+0 68	0 41x+0 II
1,4-Dichlorobenzene	0 73C-1 47	0 24x+0 23	0 29x+0 36
3 3-Dichlorobenzidine	1 23C-12 65	0 28x+7 33	0 47x+3 45
Diethyl phthalate	0 43+1 00	0 28x+1 44	0 52x+0 22
Dimethyl phthalate	0 20C+1 03	0 54x+0 19	1 05x-0 92
2 4-Dinitrotoluene	0 92C-4 81	0 12x+1 06	0 21x+1 50
2 6 Dinitrotoluene	1 06C-3 60	0 14x+1 26	0 19x+0 35
Di-n-octylphthalate	0 76C-0 79	0 21x+1 19	0 37x+1 19
Fluoranthene	0 81C+1 10	0 22x-0 73	0 28x-0 60
Fluorene	0 90C-0 00	0 12x+0 26	0 13x+0 61
Hexachlorobenzene	0 74C+0 66	0 18x-0 10	0 43x-0 52
Hexachlorobutadiene	0 71C-1 01	0 19x+0 92	0 26x+0 49
Hexachloroethane	0 73C-0 83	0 17x+0 67	0 17x+0 80
Indeno(1 2 3-cd)pyrene	0 78C-3 10	0 29x+1 46	0 50x-0 44
Isophorone	1 12C+1 41	0 27x+0 77	0 33x+0 26
Naphthalene	0 76C+1 58	0 21x-0 41	0 30x-0 68
Nitrobenzene	1 09C-3 05	0 19x+0 92	0 27x+0 21
N-Nitrosodi-n-propylamine	1 12C-6 22	0 27x+0 68	0 44x+0 47
Phenanthrene	0 87C+0 06	0 12x+0 57	0 15x+0 25
Pyrene	0 84C-0 16	0 16x+0 06	0 15x+0 31
1 2 4-Trichlorobenzene	0 94C-0 79	0 15x+0 85	0 21x+0 39
4-Chloro-3-methylphenol	0 84C+0 35	0 23x+0 75	0 29x+1 31

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser.

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
2-Chlorophenol	0 78C+0 29	0 18x+1 46	0 28x+0 97
2 4-Dichlorophenol	0 87C-0 13	0 15x+1 25	0 21x+1 28
2,4-Dimethylphenol	0 71C+4 41	0 16x+1 21	0 22x+1 31
2 4-Dinitrophenol	0 81C-18 04	0 38x+2 36	0 42x+26 29
2-Methyl-4 6-dinitrophenol	1 04C-28 04	0 10x+42 29	0 26x+23 10
2-Nitrophenol	0 07C-1 15	0 16x+1 94	6 27x+2 60
4-Nitrophenol	0 61C-1 22	0 38x+2 57	0 44x+3 24
Pentachlorophenol	0 93C+1 99	0 24x+3 03	0 30x+4 33
Phenol	0 43C+1 26	0 26x+0 73	0 35x+0 58
2 4 6-Trichlorophenol	0 91C-0 18	0 16x+2 22	0 22x+1 81

X'= Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L

s_r'= Expected single analyst standard deviation of measurements at an average concentration of x in µg/L

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in µg/L

C = True value for the concentration in µg/L

x = Average recovery found for measurements of samples containing a concentration of C in µg/L

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Table 10
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES
(EPA CLP SOW OLM 3 0)

Surrogate Compound	Water	Low/Medium Soil/Sediment
Nitrobenzene-d	35-114	23 120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-dl4	33-141	18-137
1 2-Dichlorobenzene(advisory)	16-110	20-130
Phenol-d6	10-94	24-113
2-Fluorophenol	21-100	25-121
2 4 6-Tribromophenol	10-123	19-122
2-Chlorophenol d4(advisory)	33-110	20-130

Table 11
LCS SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES
(EPA CLP SOW OLM 3 0)

Compound	%Recovery Water	RPD Water	%Recovery Soil	RPD Soil
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
1 4-Dichlorobenzene	36-97	28	28-104	27
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1 2,4 -Trichlorobenzene	39-98	28	38-107	23
4-Chloro-3-methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4 Nitrophenol	10-80	50	11-114	50
2,4-Dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Appendix 1 - Weyerhaeuser MDL Study

Matrix (soil/water) Water
MDL Aliquot 500 (ul)
Concentrated Extract Volume 500 (ul)
Injection Volume 1 0 (ul)
Units PPB (ug/L)

Date Extracted 1/9/2004
Date Analyzed 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	A	B	C	D	E	F	G
Phenol	4 69	4 86	4 13	4 62	4 45	4 65	4 73
Bis(2-chloroethyl)ether	4 85	4 35	3 82	4 58	4 37	4 41	4 78
2 Chlorophenol	4 46	4 30	3 95	4 40	4 22	4 52	4 45
1 3-Dichlorobenzene	2 74	2 30	2 36	2 76	2 90	2 89	3 29
1 4 Dichlorobenzene	2 88	2 48	2 43	2 75	3 10	2 88	3 18
1 2 Dichlorobenzene	3 13	2 66	2 79	2 97	3 24	3 06	3 58
2 Methylphenol	4 26	4 16	3 77	3 78	4 39	3 94	4 00
2 2 -oxybis(1 chloropropane)	3 68	3 57	3 17	3 51	3 53	3 61	3 77
N Nitrosodinpropylamine	4 48	4 58	3 99	4 20	4 53	4 27	4 62
4 Methylphenol	4 11	4 28	3 90	3 83	4 46	4 03	3 98
Hexachloroethane	2 20	1 83	1 86	2 14	2 37	2 33	2 70
Nitrobenzene	4 91	4 32	3 85	4 78	4 73	4 63	4 68
Isophorone	4 95	4 75	4 52	4 52	4 80	4 70	4 90
2 Nitrophenol	4 30	4 00	3 72	4 16	4 15	4 21	4 12
2 4-Dimethyphenol	2 28	2 39	2 04	1 53	3 31	1 71	1 60
Bis(2-chloroethoxy)methane	4 29	3 88	3 82	3 97	4 16	4 12	4 27
2 4-Dichlorophenol	4 49	4 50	3 96	4 50	4 56	4 36	4 43
1 2 4 Trichlorobenzene	2 92	2 53	2 63	2 95	3 26	3 03	3 32
Naphthalene	3 98	3 60	3 40	3 95	3 92	3 86	4 09
4-Chloroaniline	5 07	4 35	4 32	4 31	3 52	4 71	4 62
Hexachlorobutadiene	2 03	1 61	1 85	2 09	2 32	2 20	2 79
4-Chloro-3-Methylphenol	4 24	4 15	4 03	4 28	4 62	4 40	4 37
2 Methylnaphthalene	3 84	3 40	3 44	3 75	3 96	3 72	4 16
Hexachlorocyclopentadiene	<1	<1	<1	<1	<1	<1	<1
2 4 6 Trichlorophenol	4 51	4 35	4 17	4 38	4 22	4 20	4 31
2 4 5-Trichlorphenol	4 35	4 06	3 86	3 98	4 41	4 18	4 27
2 Chloronaphthalene	3 97	3 69	3 50	3 93	4 03	3 78	4 20
2 Nitroaniline	5 24	3 91	4 87	4 80	4 21	5 00	4 93
Acenaphthylene	4 24	4 08	3 90	4 33	4 31	4 31	4 36
2 6 Dinitrotoluene	4 88	4 20	4 49	4 52	4 64	4 75	4 66
3-Nitroaniline	4 48	4 39	4 54	4 63	4 59	4 76	4 66
Acenaphthene	4 23	3 92	3 74	4 12	4 23	4 16	4 23
2 4 Dinitrophenol	5 87	5 79	6 37	6 29	6 46	6 56	5 94
Dibenzofuran	4 49	3 96	4 18	4 50	4 47	4 47	4 45
4 Nitrophenol	5 42	4 86	5 56	5 67	5 94	5 68	5 34
2 4 Dinitrotoluene	5 16	4 51	5 28	5 11	5 13	5 13	5 27
Fluorene	4 51	3 85	4 16	4 41	4 58	4 58	4 52
Dimethylphthalate	4 98	4 46	4 61	4 60	4 61	4 64	4 71
Diethylphthalate	4 79	4 36	4 75	4 63	4 70	4 72	4 74
4 Chlorophenyl phenylether	4 40	3 63	4 05	4 38	4 39	4 41	4 37

Matrix (soil/water) Water
MDL Aliquot 500 (ul)
Concentrated Extract Volume 500 (ul)
Injection Volume 1 0 (ul)
Units PPB (ug/L)

Date Extracted 1/9/2004
Date Analyzed 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	A	B	C	D	E	F	G
4 Nitroaniline	4 96	3 71	4 96	5 13	4 81	5 30	5 14
4 6-Dinitro-2 methylphenol	5 36	5 54	5 78	5 71	5 72	5 89	5 40
N Nitrosodiphenylamine	4 93	4 70	4 59	4 54	3 49	4 75	5 04
4 Bromophenyl phenylether	5 09	5 05	4 70	4 86	4 69	5 14	5 01
Hexachlorobenzene	5 13	5 03	4 51	4 70	5 07	4 88	4 98
Pentachlorophenol	5 64	6 04	5 94	6 23	6 50	6 44	6 07
Phenanthrene	5 29	4 94	4 93	5 10	5 24	5 15	5 24
Anthracene	5 01	4 75	4 84	4 98	4 87	5 24	5 01
Di-n-Butylphthalate	5 53	5 36	5 65	5 42	5 61	5 59	5 59
Fluoranthene	4 65	4 22	4 87	4 90	4 93	4 93	4 66
Pyrene	6 02	6 47	5 84	5 58	5 30	5 98	5 90
Butylbenzylphthalate	5 37	5 52	5 35	5 13	4 86	5 31	5 29
Benzo(a)Anthracene	5 38	5 34	5 40	5 30	5 14	5 45	5 47
3 3 Dichlorobenzidine	3 30	2 87	3 04	2 86	0 51	2 72	3 03
Chrysene	5 56	5 57	5 56	5 50	5 34	5 52	5 80
bis(2-ethylhexyl)Phthalate	5 60	5 53	5 70	5 03	5 07	5 23	5 56
Di-n-octylphthalate	4 88	5 05	5 02	4 76	4 71	4 90	4 81
Benzo(b)fluoranthene	4 79	4 74	4 95	4 54	4 46	4 66	4 66
Benzo(k)fluoranthene	4 85	4 81	4 80	4 89	5 06	4 98	5 38
Benzo(a)pyrene	4 57	4 39	4 45	4 35	4 27	4 52	4 55
Indeno(1 2 3 cd)pyrene	4 54	4 45	4 49	4 48	4 60	4 51	4 47
Dibenzo(a h)anthracene	4 43	4 43	4 40	4 26	4 41	4 38	4 39
Benzo(g h i)perylene	4 81	4 71	4 74	4 62	4 78	4 66	4 78
Carbazole	6 01	5 12	5 70	6 08	5 49	6 17	5 79
Aniline	4 89	4 96	4 70	4 12	1 48	4 95	4 65
Benzyl Alcohol	5 37	5 28	4 81	4 94	5 20	5 12	5 40
Benzoic Acid	4 77	5 11	4 93	5 12	6 07	5 22	4 87
Benzidine	<10	<10	<10	<10	<10	<10	<10
1 2 Diphenylhydrazine	4 99	5 10	4 61	4 82	4 62	4 86	5 06

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Matrix (soil/water) Water
MDL Aliquot 500 (ul)
Concentrated Extract Volume 500 (ul)
Injection Volume 1 0 (ul)
Units PPB (ug/L)

Date Extracted 1/9/2004
Date Analyzed 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	MEAN	STDEV	MDL	SPIKE	% Rec
Phenol	4 59	0 237	0 7	5	92
Bis(2 chloroethyl)ether	4 45	0 342	1 1	5	89
2 Chlorophenol	4 33	0 196	0 6	5	87
1 3-Dichlorobenzene	2 75	0 339	1 1	5	55
1 4 Dichlorobenzene	2 81	0 285	0 9	5	56
1 2 Dichlorobenzene	3 06	0 302	1 0	5	61
2 Methylphenol	4 04	0 237	0 7	5	81
2 2 -oxybis(1-chloropropane)	3 55	0 190	0 6	5	71
N Nitrosodinpropylamine	4 38	0 233	0 7	5	88
4 Methylphenol	4 08	0 221	0 7	5	82
Hexachloroethane	2 20	0 303	1 0	5	44
Nitrobenzene	4 56	0 361	1 1	5	91
Isophorone	4 73	0 169	0 5	5	95
2 Nitrophenol	4 09	0 188	0 6	5	82
2 4-Dimethyphenol	2 12	0 620	1 9	5	42
Bis(2-chloroethoxy)methane	4 07	0 186	0 6	5	81
2 4-Dichlorophenol	4 40	0 204	0 6	5	88
1 2 4 Trichlorobenzene	2 95	0 294	0 9	5	59
Naphthalene	3 83	0 242	0 8	5	77
4 Chloroaniline	4 41	0 480	1 5	5	88
Hexachlorobutadiene	2 13	0 373	1 2	5	43
4 Chloro-3-Methylphenol	4 30	0 190	0 6	5	86
2 Methylnaphthalene	3 75	0 271	0 9	5	75
Hexachlorocyclopentadiene	<1	N M	N M	5	N M
2 4 6-Trichlorophenol	4 31	0 120	0 4	5	86
2 4 5-Trichlorphenol	4 16	0 201	0 6	5	83
2 Chloronaphthalene	3 87	0 233	0 7	5	77
2 Nitroaniline	4 71	0 472	1 5	5	94
Acenaphthylene	4 22	0 168	0 5	5	84
2 6-Dinitrotoluene	4 59	0 218	0 7	5	92
3 Nitroaniline	4 58	0 122	0 4	5	92
Acenaphthene	4 09	0 190	0 6	5	82
2 4 Dinitrophenol	6 18	0 310	1 0	5	124
Dibenzofuran	4 36	0 209	0 7	5	87
4 Nitrophenol	5 50	0 342	1 1	5	110
2 4-Dinitrotoluene	5 08	0 262	0 8	5	102
Fluorene	4 37	0 273	0 9	5	87
Dimethylphthalate	4 66	0 160	0 5	5	93
Diethylphthalate	4 67	0 145	0 5	5	93
4 Chlorophenyl phenylether	4 23	0 295	0 9	5	85

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Matrix (soil/water) Water
MDL Aliquot 500 (ul)
Concentrated Extract Volume 500 (ul)
Injection Volume 1 0 (ul)
Units PPB (ug/L)

Date Extracted 1/9/2004
Date Analyzed 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	MEAN	Std Dev	MDL	Amount Spiked	% Recovery
4 Nitroaniline	4 86	0 531	1 7	5	97
4 6 Dinitro-2 methylphenol	5 63	0 199	0 6	5	113
N Nitrosodiphenylamine	4 58	0 511	1 6	5	92
4-Bromophenyl phenylether	4 93	0 185	0 6	5	99
Hexachlorobenzene	4 90	0 223	0 7	5	98
Pentachlorophenol	6 12	0 297	0 9	5	122
Phenanthrene	5 13	0 146	0 5	5	103
Anthracene	4 96	0 158	0 5	5	99
Di n Butylphthalate	5 54	0 107	0 3	5	111
Fluoranthene	4 74	0 258	0 8	5	95
Pyrene	5 87	0 366	1 2	5	117
Butylbenzylphthalate	5 26	0 211	0 7	5	105
Benzo(a)Anthracene	5 35	0 111	0 3	5	107
3 3 Dichlorobenzidine	2 62	0 948	3 0	5	52
Chrysene	5 55	0 136	0 4	5	111
bis(2-ethylhexyl)Phthalate	5 39	0 273	0 9	5	108
Di n-octylphthalate	4 88	0 127	0 4	5	98
Benzo(b)fluoranthene	4 69	0 162	0 5	5	94
Benzo(k)fluoranthene	4 97	0 205	0 6	5	99
Benzo(a)pyrene	4 44	0 112	0 4	5	89
Indeno(1 2 3 cd)pyrene	4 51	0 051	0 2	5	90
Dibenzo(a h)anthracene	4 39	0 059	0 2	5	88
Benzo(g h i)perylene	4 73	0 069	0	5	95
Carbazole	5 77	0 370	1 2	5	115
Aniline	4 25	1 26	3 9	5	85
Benzyl Alcohol	5 16	0 220	0 7	5	103
Benzoic Acid	5 16	0 433	1 4	5	103
Benzidine	<10	N M	N M	5	N M
1 2 Diphenylhydrazine	4 87	0 198	0 6	5	97

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Appendix 2 - TYPICAL SURROGATE AND LCS PERCENT RECOVERIES

PRECISION & ACCURACY
STUDY 8270

Date 03/07/94
Data 2SV40304A-2SV40304E
Method 8270
Analyst J Leong

Extractionist T Sutherland
Extractionist M Luthy
Extraction Date 2/22/94
Spiked 50µg/L

Replicate #	#1	#2	#3	#4	average (X) (% rec)	Std Dev (s)	complian ce	limit for s	Range for X (% rec)	Range for P
	% recovery (P)									
PHENOL	53 7	55 5	53 9	58 3	55 4	2 1	Y	22 6	16 6-100 0	5-112
BIS(2-CHLOROETHYL)ETHER	73 9	78 1	78 9	69 2	75 0	4 4	Y	55	42 9-126 0	12-158
2-CHLOROPHENOL	62 4	65 2	61 1	65 1	63 4	2 0	Y	28 7	36 2-120 4	23-134
1 3-DICHLOROBENZENE	60 0	72 6	72 2	62 4	66 8	6 5	Y	41 7	16 7-153 9	d-172
1 4-DICHLOROBENZENE	61 8	72 0	72 0	62 9	67 1	5 6	Y	32 1	37 3-105 7	20-124
1 2-DICHLOROBENZENE	62 5	70 4	69 4	62 3	66 1	4 3	Y	30 9	48 6-112 0	32-129
2-METHYLPHENOL	73 8	77 5	74 2	74 4	75 0	1 7		NA		
2 2'-OXYBIS(1-CHLOROPROPANE)	83 1	86 7	84 8	74 7	82 3	5 3	Y	46 3	62 8-138 6	36-166
4-METHYLPHENOL	75 8	74 7	76 2	77 1	76 0	1 0		NA		
N-NITROSO-DI-N-PROPYLAMINE	79 4	81 5	81 9	73 2	79 0	4 0	Y	55 4	13 6-197 9	d-230

HEXACHLOROETHANE	57 3	75 6	75 4	65 6	68 5	8 8	Y	24 5	55 2-100 0	40-113
NITROBENZENE	73 6	78 0	75 8	67 2	73 6	4 7	Y	39 3	54 3-157 6	35-180
ISOPHORONE	79 7	82 3	83 4	73 5	79 7	4 4	Y	63 3	46 6-180 2	21-196
2-NITROPHENOL	78 4	82 7	78 4	84 7	81 0	3 1	Y	35 2	45 0-166 7	29-182
2 4-DIMETHYLPHENOL	59 9	52 4	63 8	50 1	56 5	6 4	Y	26 1	41 8-109 0	32-119
BIS(2-CHLOROETHOXY)METHANE	82 3	84 5	85 0	75 8	81 9	4 2	Y	34 5	49 2-164 7	33-184
2 4-DICHLOROPHENOL	72 3	76 5	72 0	77 6	74 6	2 9	Y	26 4	52 5-121 7	39-135
1 2 4-TRICHLOROBENZENE	70 0	81 0	80 5	71 0	75 6	5 9	Y	28 1	57 3-129 2	44-142
NAPHTHALENE	73 8	79 2	79 9	69 6	75 6	4 9	Y	30 1	35 6-119 6	21-133
4-CHLOROANILINE	78 3	81 3	83 7	72 9	79 0	4 7		NA		
HEXACHLOROBUTADIENE	66 0	82 6	81 9	71 3	75 4	8 2	Y	26 3	37 8-102 2	24-116
4-CHLORO-3-METHYLPHENOL	76 5	78 7	77 9	77 2	77 5	0 9	Y	37 2	40 8-127 9	22-147
2-METHYLNAPHTHALENE	77 6	80 3	81 9	74 7	78 6	3 2		NA		
HEXACHLOROCYCLOPENTADIENE	3 0	2 4	4 1	3 9	3 4	0 8		NA		
2 4 6-TRICHLOROPHENOL	77 8	81 4	73 9	83 3	79 1	4 1	Y	31 7	52 4-129 2	37-144
2 4 5-TRICHLOROPHENOL	76 7	76 0	70 8	74 9	74 6	2 7		NA		
2-CHLORONAPHTHALENE	80 2	84 1	84 9	77 4	81 6	3 5	Y	13 0	64 5-113 5	60-118
2-NITROANILINE	78 4	81 3	83 5	74 2	79 3	4 0		NA		
DIMETHYLPHTHALATE	36 4	68 3	71 9	67 5	61 0	16 5	Y	23 2	d-100 0	d-112
ACENAPHTHYLENE	76 4	79 3	81 0	73 7	77 6	3 2	Y	40 2	53 5-126 0	33-145

2 6-DINITROTOLUENE	80 9	85 9	90 2	80 7	84 4	4 6	Y	29 6	68 1-136 7	50-158
3-NITROANILINE	88 9	92 9	95 6	88 4	91 5	3 4		NA		
ACENAPHTHENE	77 4	80 3	80 3	73 0	77 8	3 4	Y	27 6	60 1-132 3	47-145
2 4-DINITROPHENOL	81 1	86 3	79 6	92 0	84 7	5 6	Y	49 8	d-172 9	d-191
4-NITROPHENOL	73 8	78 2	67 0	74 9	73 5	4 7	Y	47 2	13 0-106 5	d-132
DIBENZOFURAN	79 5	83 0	85 0	76 6	81 0	3 7		NA		
2 4-DINITROTOLUENE	82 1	83 8	87 7	80 7	83 6	3 0	Y	21 8	47 5-126 9	39-139
DIETHYLPHTHALATE	74 5	87 6	92 2	86 0	85 1	7 5	Y	26 5	d-100 0	d-114
4-CHLOROPHENYLPHENYLETHER	88 9	93 1	95 6	87 7	91 3	3 7	Y	33 4	38 4-144 7	25-158
FLUORENE	80 8	81 8	85 8	78 6	81 7	3 0	Y	20 7	71 6-108 4	59-121
4-NITROANILINE	86 6	96 3	98 2	92 5	93 4	5 1		NA		
4 6-DINITRO-2-METHYLPHENOL	73 9	76 9	72 1	78 3	75 3	2 8	Y	93 2	53 0-100 0	d-181
N-NITROSODIPHENYLAMINE	78 5	96 4	98 6	90 5	91 0	9 0		NA		
4-BROMOPHENYLPHENYLETHER	94 6	98 3	101 3	91 8	96 5	4 2	Y	23	64 9-114 4	53-127
HEXACHLOROBENZENE	90 2	94 9	98 3	88 7	93 0	4 4	Y	24 9	7 8-141 5	d-152
PENTACHLOROPHENOL	86 9	92 0	82 1	92 7	88 5	4 9	Y	48 9	38 1-151 8	14-176
PHENANTHRENE	82 1	83 9	86 2	77 7	82 5	3 6	Y	20 6	65 2-108 7	54-120
ANTHRACENE	84 5	86 5	90 0	80 4	85 4	4 0	Y	32	43 4-118 0	27-133
CARBAZOLE	118 8	127 5	133 2	123 5	125 8	6 1		NA		
DI-N-BUTYLPHTHALATE	87 2	92 0	96 7	86 1	90 5	4 9	Y	16 7	8 4-111 0	1-118
FLUORANTHENE	82 0	85 2	88 1	79 5	83 7	3 8	Y	32 8	42 9-121 3	26-137
PYRENE	86 1	91 1	87 1	82 1	86 6	3 7	Y	25 2	69 6-100 0	52-115

BUTYLBENZYLYPHTHALATE	88 0	95 8	91 6	84 7	90 0	4 7	Y	23 4	d-139-9	d-152
3,3'-DICHLOROBENZIDENE	129 4	150 0	146 8	132 3	139 6	10 3	Y	71 4	8 2-212 5	d-262
BENZO(A)ANTHRACENE	83 2	93 6	84 3	82 2	85 8	5 3	Y	27 6	41 8-133 0	33-143
CHRYSENE	83 1	88 7	88 2	80 9	85 2	3 8	Y	48 3	44 1-139 9	17-168
BIS(2-ETHYLHEXYL)PHTHLATE	88 0	94 7	90 3	83 0	89 0	4 9	Y	41 1	28 9-136 8	8-158
DIOCTYLPHTHALATE	81 9	83 8	89 6	79 0	83 5	4 5	Y	31 4	18 6-131 8	4-146
BENZO(B)FLUORANTHENE	79 9	83 7	85 6	77 1	81 6	3 8	Y	38 8	42 0-140 4	24-159
BENZO(K)FLUORANTHENE	73 8	70 3	79 0	72 0	73 8	3 7	Y	32 3	25 2-145 7	11-162
BENZO(A)PYRENE	79 7	81 4	85 2	78 6	81 2	2 9	Y	39	31 7-148 0	17-163
INDENO(1 2 3-CD)PYRENE	84 3	92 0	88 8	82 4	86 9	4 4	Y	44 6	d-150 9	d-171
DIBENZ(A H)ANTHRACENE	86 0	93 5	94 7	86 7	90 2	4 5	Y	70	d-199 7	d-227
BENZO(G H I)PERYLENE	80 6	83 5	88 2	80 1	83 1	3 7	Y	58 9	d-195 0	d-219

Appendix 3 - METHOD MODIFICATIONS FOR MARINE SEDIMENT "PSEP"

INTRODUCTION – Analytical Method AM E-8270 requires modifications to address specific low reporting limits and reporting units

MODIFICATIONS – The following modifications are required

I EXTRACTION PROCEDURE RECOMMENDATION
II ORGANIC CARBON
III REPORTING LIMITS
IV SAMPLE AMOUNT
V EXTRACTION MODIFICATIONS
VI CALIBRATION STANDARDS
VII REPORTING UNITS

I EXTRACTION PROCEDURE RECOMMENDATION

The recommended extraction method for marine sediments is soxhlet extraction SOP AC G-3540 Ultrasonic extraction SOP AC G-3350 is an acceptable alternative however comparable recoveries to SOP AC G-3540 must be confirmed

II ORGANIC CARBON

A Numerical reporting values for organic analytes will be normalized based on organic carbon

B The analysis for total organic carbon as well as the percent moisture will be performed by Group 4 (Conventional Group)

C Total organic carbon and percent moisture data will be used to calculate sample size

III REPORTING LIMITS

The reporting limits for marine sediment is analyte specific The reporting limits are detailed in Table A1 However, a 380-µg/kg organic carbon reporting limit will be used as the basis for determining sample size final sample extract volume, and calibration standard concentration

IV SAMPLE AMOUNT

Use the following formula to determine sample size

$$\text{Sample size (g)} = \frac{(LS)(F_v)(2)}{(380)(D)(TOC)}$$

Where

LS = Concentration of the lowest calibration standard in ug/mL For marine sediment the low calibration standard concentration is 1 0 ug/mL

F_V = Final volume of the sample extract For marine sediment the final extract volume is 250 microliters

The value of 2 is used due to GPC loop loss

The value of 380 is the resultant analyte concentration in PPB OC normalized (specified reporting limit)

D = (100 - % moisture in sample)/100

TOC = percent total organic carbon in the dry weight sample (1 percent TOC = 0 01)

V EXTRACTION MODIFICATIONS

If the calculated sample size is greater than 60 g the following extraction modifications will need to be made

A Weigh the sample into two equal portions Spike each portion with one half of the surrogate solution and/or spiking solution For example, suppose the total sample size is 150 g and one mL of spiking solution is required The procedure modification would require two sample portions weighing 75 g each 500 µL of the spiking solution would be added to each sample portion

B Combine the sample fraction extracts prior to sample concentration

C After GPC cleanup concentrate the sample extract to 200 µL Transfer the sample extract to an amber GC vial containing a 300 µL GC vial insert (or equivalent insert) Rinse the concentration tube with small amounts of methylene chloride and combine with the extract in the insert Continue until a final extract volume of 250 µL is achieved

VI CALIBRATION STANDARDS

Include an initial calibration standard at a concentration of 1 0 µg/mL Verify the curves are valid for the following analytes 1 2-dichlorobenzene 1 4-dichlorobenzene 1 2 4-trichlorobenzene hexachlorobenzene

VII REPORTING UNITS

Report the analyte concentration in mg/kg TOC Include the concentration for LPAH, HPAH compounds and total benzofluoranthenes The LPAH criterion represents the sum of the following low molecular polynuclear aromatic hydrocarbon compounds naphthalene acenaphthylene acenaphthene fluorene phenanthrene, and anthracene The HPAH criterion represents the sum of the following high molecular polynuclear aromatic hydrocarbon compounds fluoranthene pyrene benz(a)anthracene chrysene total benzofluoranthenes, benzo(a)pyrene, indeno(1 2 3 cd)pyrene dibenz(a h)anthracene and benzo(g h i)perylene The total benzofluoranthenes criterion represents the sum of the concentrations of B, J " and "K isomers

Table A1 Reporting limits for marine sediment

Chemical Parameter	mg/kg Organic Carbon
LPAH	370
Naphthalene	99
Acenaphthylene	66
Acenaphthene	16
Fluorene	23
Phenanthrene	100
Anthracene	220

Chemical Parameter	mg/kg Organic Carbon
Bis(2-ethylhexyl) Phthalate	47
Di-n-octyl Phthalate	58
Dibenzofuran	15
Hexachlorobutadiene	3 9
N-Nitrosodiphenylamine	11

Chemical Parameter	mg/kg Organic Carbon
2-Methylnaphthalene	38
HPAH	960
Fluoranthene	160
Pyrene	1000
Benz(a)anthracene	110
Chrysene	110
Total Benzofluoranthene	230
Benzo(a)pyrene	99
Indeno(1 2 3 cd)pyrene	34
Dibenz(a h)anthracene	12
Benzo(g h i)perylene	31
1 2-Dichlorobenzene	2 3
1 4-Dichlorobenzene	3 1
1 2,4-Trichlorobenzene	0 81
Hexachlorobenzene	0 38
Dimethyl Phthalate	53
Diethyl Phthalate	61
Di-n-butyl Phthalate	220
Butyl Benzyl Phthalate	4 9

Chemical Parameter	mg/kg Organic Carbon
Chemical Parameter	µg/kg Dry Weight(PPB)
Phenol	420
2-Methylphenol	63
4-Methylphenol	670
2 4-Dimethyl Phenol	29
Pentachlorophenol	360
Benzyl Alcohol	57
Benzoic Acid	650

1 0 SCOPE

1 1 The SPLP is designed to determine the mobility of both organic and inorganic analytes present in liquid solid and multiphasic wastes

1 2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded the SPLP extraction itself need not be run

1 3 If an analysis of any one of the liquid fractions of the SPLP extract indicates that a regulated compound is present at such high concentrations that even after accounting for dilution from the other fractions of the extract the concentration would be equal to or above the regulatory level for that compound then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract

1 4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte equals or exceeds the regulatory level for that compound then the waste is hazardous and extraction using the ZHE is not necessary However extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level

2 0 SUMMARY OF METHOD

2 1 For liquid wastes (i e those containing less than 0 5 % dry solid material) the waste after filtration through a 0 6 - 0 8 um glass fiber filter is defined as the SPLP extract

2 2 For wastes containing greater than or equal to 0 5 % solids the liquid if any is separated from the solid phase and stored for later analysis the particle size of the solid phase is reduced if necessary The solid phase is extracted with an amount of extraction fluid equal to 20 times the mass of the solid phase The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil If the sample is a waste or wastewater, the extraction fluid employed is a pH 4 2 solution A special extractor vessel is used when testing for volatile analytes Following extraction, the liquid extract is separated from the solid phase by filtration through a 0 6 - 0 8 um glass fiber filter

2 3 If compatible (i e multiple phases will not form on combination) the initial liquid phase of the waste is added to the liquid extract and these are analyzed together If incompatible the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration

3 0 INTERFERENCES

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods The pH of the extraction fluid has the greatest impact on the metals results and therefore the extraction fluid must have the pH within ± 0 05 of the specified pH Poor precision is due to sample homogeneity

4 0 ESTIMATE OF ANALYTICAL TIME

This method has an 18 hour extraction and therefore can take up to 24 hours

5 0 AMOUNT OF SAMPLE REQUIRED

The SPLP places requirements on the minimal size of the sample depending upon the physical state of the waste and the analytes of concern A 5-gram aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure Another 100- to 10,000-g aliquot may be needed to actually conduct the nonvolatile extraction If volatile organics are of concern another 25- to 500-g aliquot may be needed Quality control measures may require additional aliquots Further extra sample should be collected just in case something goes wrong with the initial attempt to conduct the test

6 0 SAMPLING, SAMPLE HANDLING, AND PRESERVATION

6 1 Vinyl gloves will be worn when handling samples If a sample produces a noxious odor try to work with the sample in a hood

6 2 Preservatives shall not be added to samples before extraction

6 3 Samples are refrigerated unless refrigeration results in irreversible physical change to the waste If precipitation occurs the entire sample (including precipitate) should be extracted

6 4 When the waste is to be evaluated for volatile analytes care shall be taken to minimize the loss of volatiles Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e g stored at 4 °C and opened only immediately prior to extraction)

6 5 SPLP extracts should be prepared for analysis and analyzed within the prescribed holding times Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs in which case samples must be refrigerated at 4 °C Extracts should be kept at 4 °C for organic non-volatiles analytes according to the guidance given in the individual analysis methods Extracts or portions of extracts for VOA analyte determinations shall not be allowed to come into contact with the atmosphere (i e no headspace) to prevent losses and kept at 4 °C

6 6 Prepared samples (digestates) will be stored for 1 month and then dumped into the disposal drum When the disposal drum is full it will be transferred to the chemical management unit for proper disposal

7 0 EQUIPMENT REQUIRED

7 1 A rotation device that can rotate the extraction vessel end-over-end at 30 ± 2 rpm The rotation device used by this lab is the 6-vessel model no 3740 6, from Associated Design and Manufacturing Co

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

7 2 Extraction vessels for organic non-volatiles must be glass Plastic extraction vessels can be used if only metallic analytes are required

The Zero-Headspace Extraction (ZHE) vessel is used when the waste is being tested for the mobility of volatile analytes (VOA) The ZHE vessel allows for liquid/solid separation within the device, and effectively precludes headspace This vessel allows for initial liquid/solid separation extraction and final extract filtration without opening the vessel For the ZHE vessel to be acceptable for use the piston within the vessel should be able to be moved with approximately 15 psi or less If it takes more pressure to move the piston, the O-rings in the device should be replaced If this does not solve the problem the ZHE vessel is unacceptable for TCLP analyses The vessel has an internal volume of 500 600 mL and is equipped to accommodate a 90-110 mm filter This lab uses a ZHE Model 3745-ZHE from Associated Design and Manufacturing Co

The ZHE vessel is used for filtration and shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation up to 50 psi

7 3 The filtering device for extractions other than the VOA can be any device with a minimum internal volume of 300-mL capable of supporting a 47-mm diameter glass fiber filter and able to withstand the pressure needed to accomplish separation up to 50 psi The filtering device used by this lab is the Millipore Corporation Model YT30142HW with a 1500-mL internal volume and requires a 142-mm diameter filter

7 4 Filters are borosilicate glass fiber contain no binder materials and have an effective pore size of 0 6 - 0 8 µm Glass fiber filters are fragile and should be handled with care The filters used by this lab for non-VOA extractions are the Whatman, Glass Microfibre Filters - Acid Treated Low Metal 142 mm 0 6 - 0 8 µm cat no 1810-142 For VOA extractions the lab uses Pall Life Sciences Glass Fiber Filters 90 mm 0 7 µm p/n 66256

7 5 Glass syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device This lab uses the Model 3775 stainless steel 600-mL gas-tight syringe to collect initial and final filtrates forming the SPLP ZHE extract and to add extraction fluid A peristaltic pump capable of transferring the extraction fluid into the ZHE vessel without changing the nature of the extraction fluid can also be used

8 0 REAGENTS

Reagents must not contain detectable analytes of interest NOTE All references to water in this method refer to organic-free water from lab NLM-228

8 1 Sulfuric acid/nitric acid (60/40 weight percent mixture sulfuric/nitric acid

Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid with stirring in an Erlenmeyer flask standing in an ice bath

Sulfuric acid (conc)

Sulfuric acid [7664-93-9]

DANGER Degree of hazard depends upon concentration Conc acid mainly refers to those over 52 %

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Handle with care Wear safety goggles neoprene gloves and a plastic apron Use in a hood if mist or fumes generated Conc sulfuric acid is a strong corrosive acid and can cause severe burns Very carefully add acid to water with frequent or continuous stirring Mix in a tub or stoppered sink Upon dilution in water the generation of heat could cause it to erupt and spatter over a large area Proceed with caution
Conc sulfuric acid is extremely destructive to tissue of the mucous membranes and upper respiratory tract eyes and skin
Inhalation of mist or heated fumes may result in spasm inflammation and edema of the larynx and bronchi chemical pneumonitis and pulmonary edema Symptoms of exposure may include burning sensation or irritation of the nose and throat coughing wheezing laryngitis shortness of breath, labored breathing, headache nausea and vomiting
Avoid skin contact Conc acid is extremely corrosive Symptoms of redness pain, and severe burn can occur Circulatory collapse with clammy skin weak and rapid pulse shallow respirations and scanty urine may follow skin contact or ingestion Circulatory shock is often the immediate cause of death
Avoid eye contact Extremely corrosive Sulfuric acid can cause severe irritation or burns and result in permanent damage Contact can cause blurred vision redness pain and severe tissue burns Strong concentrations will probably cause blindness
Long term exposure may cause erosion of teeth
Sulfuric acid is an oxidizer and strong dehydrating agent May cause ignition of finely divided organic materials on contact Reacts with most metals to produce hydrogen gas which can form an explosive mixture with air Keep away from bases carbides chlorates fulminates nitrates picrates cyanides alkali halides zinc iodide permanganates hydrogen peroxide azides perchlorates nitromethane phosphorous nitrites halogens metal acetylides oxides and hydrides, metals (especially finely powdered ones--yields hydrogen gas) strong oxidizing and reducing agents water and many other reactive substances
Reaction products include hydrogen, from reaction with metals or sulfur oxide fumes when heated
Permissible exposure limit (PEL) is 1 mg/m^3
Mist is a known carcinogen depending on duration and level of exposure

Nitric acid

Nitric acid (concentrated), HNO_3 CAS # 7697-37-2

DANGER Handle with care Wear safety glasses vinyl gloves lab coat and use in a hood Conc nitric acid is a strong corrosive acid and liquid and vapor can cause severe burns Carefully add acid to water with frequent or continuous stirring Upon dilution in water the generation of heat could cause it to erupt and spatter over a large area Proceed with caution
Harmful if inhaled and may cause delayed lung injury If inhaled can cause severe irritation or burns of mucous membranes and respiratory system resulting in coughing difficult breathing chest pains pneumonia pulmonary edema lung inflammation unconsciousness and may be fatal Can cause severe ulceration
Skin contact can cause severe irritation redness pain and severe skin burns Concentrated acid causes deep ulcers and stain skin a yellow or yellow brown color
Eye contact can cause severe irritation or burns and result in permanent damage
Long term exposure to concentrated vapors may cause erosion of teeth
Nitric acid is a strong oxidizer Contact with combustible materials flammable materials such as wood and solvents or powdered metals can cause fire or explosion Reacts with most metals to produce hydrogen gas which can form an explosive mixture with air Keep away from strong bases carbides carbonates charcoal (hydrogen) sulfides cyanides combustible materials combustible organics or organic materials turpentine strong reducing agents most common metals carbides ammonium hydroxide water and alcohols

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

Certain mixtures with benzene 1 2 dichloroethane or dichloromethane may be detonatable
Reaction products include highly toxic and dangerous fumes of reddish oxides of nitrogen having the equivalent affects as those noted above
Short term exposure limit (STEL) is 10 mg/m^3 (4 ppm) and permissible exposure limit (PEL) is 5 mg/m^3 (2 ppm)

8 3 Extraction fluid

8 3 1 Extraction fluid # 1 Add the 60/40 weight percent mixture of sulfuric/nitric acid solution (8 1) to reagent water until the pH is 4 20 ± 0 05 The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River and the leachability of wastes and wastewaters

NOTE Solutions are unbuffered and exact pH may not be attained

8 3 2 Extraction fluid # 2 Add the 60/40 weight percent mixture of sulfuric/nitric acid solution (8 1) to reagent water until the pH is 5 00 ± 0 05 The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River

8 3 3 Extraction fluid # 3 Reagent water used to determine cyanide and volatiles leachability

NOTE These extraction fluids should be monitored frequently for impurities The pH should be checked prior to use to ensure that these fluids are made up accurately If impurities are found or the pH is not within the above specifications the fluid shall be discarded and fresh extaction fluid prepared

8 4 Solution preparation

8 4 1 Solutions will be prepared following established recipes located in a solution prep log book All solution prep will be recorded in a log book noting any variations to a recipe as needed If a recipe does not exist the prep log must state the volume lot number and expiration date of the stock solutions used as well as the final volume and expiration date of the prepared solution

8 5 Compressed N_2 gas

9 0 PROCEDURE

Note All weighing shall be measured to the nearest 0 1 gram

9 1 Determine the percent solids of the waste that are liquid or multiphasic liquid/solid Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure

9 1 1 Pre-weigh a filter and a container that will receive the filtrate to the nearest 0 001 g Place the filter in the filtering device

9 1 2 Weigh a 100-g minimum aliquot of the sample and record the mass Try to use an amount that will produce 100 g of solids Allow slurries to stand to permit the solid phase to settle Wastes that settle slowly may be centrifuged prior to filtration Centrifugation is to be used only as an aid to filtration If used the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system

9 1 3 Transfer the aliquot to the filtering device and spread evenly over the surface of the filter If filtering the waste at 4 °C will reduce the amount of expressed liquid over what would be

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering If waste material (> 1 % of original sample mass) has adhered to the container used to transfer the sample to the filtration apparatus determine the mass of this residue and subtract it from the sample mass to determine the actual mass of the sample that will be filtered

9 1 4 Gradually apply vacuum pressure up to 10 psi and when no additional liquid has passed through the filter in a 2-min interval slowly increase the pressure in 10 psi increments to a maximum of 50 psi waiting at each 10-psi increment until a 2-min interval in which liquid does pass through the filter is reached When the flow has ceased for 2 min at 50 psi stop the filtration The material in the filter holder is defined as the solid phase of the waste and the filtrate is defined as the liquid phase

NOTE Some wastes such as oily wastes and some paint wastes will obviously contain some material that appears to be a liquid Even after applying vacuum or pressure filtration this material may not filter If this is the case, the material within the filtration device is defined as a solid Do not replace the original filter with a fresh filter under any circumstances Use only one filter

9 1 5 Determine the mass of the liquid phase by subtracting the mass of the filtrate container from the total mass of the filtrate-filled container Determine the mass of the solid phase of the waste sample by subtracting the mass of the liquid phase from the mass of the total waste sample

9 1 6 Calculate the percent solids as follows % solids = mass of solids + sample mass x 100

9 1 7 If the percent solids is ≥ 0 5 % then proceed to determine whether the solid material requires particle size reduction If the percent solids is < 0 5 %, then the filtrate is the extract

9 2 Determine if the solid portion of the waste requires particle size reduction Particle size reduction is required unless the solid is smaller than 1 cm in its narrowest dimension (i e is capable of passing through a 9 5-mm standard sieve) Reduce the particle size by crushing cutting or grinding the waste to a particle size smaller than 1 cm in its narrowest dimension

If the solids are prepared for organic volatiles extraction, special precautions must be taken Wastes and appropriate reduction equipment should be refrigerated, if possible to 4 °C prior to particle size reduction The means used to effect particle size reduction must not generate heat in and of itself If reduction of the solid phase of the waste is necessary exposure of the waste to the atmosphere should be avoided to the extent possible

9 3 Determine the appropriate extraction fluid to use for the non-volatiles extraction as follows

NOTE SPLP extraction for volatiles uses only extraction fluid #3

9 3 1 Aliquot 5 0 g of the solid phase of the waste into a 500-mL beaker

9 3 2 Add 96 5 mL of DDI-water to the beaker cover with a watchglass and stir vigorously for 5 min using a magnetic stirrer

9 3 3 Measure and record the pH If the pH is < 5 0 use extraction fluid #1 If the pH is > 5 0 add 3 5 mL 1N nitric acid slurry briefly cover with a watchglass heat to 50 °C and hold for 10 min

9 3 4 Let the solution cool to room temperature and record the pH If the pH is < 5 0 use extraction fluid #1 If the pH is > 5 0, use extraction fluid #2

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

9 4 **SPLP extraction procedure when volatiles are not involved**
A minimum sample size of 100 g (solid and liquid phases) is recommended In some cases a larger sample size may be appropriate, depending on the percent solids of the waste, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid and whether inorganics semivolatile organics pesticides and herbicides are all analytes of concern Enough solids should be generated for extraction such that the volume of SPLP extract will be sufficient to support all of the analyses required If the amount of extract generated by a single SPLP extraction will not be sufficient to perform all of the analyses more than one extraction may be performed and the extracts from each combined and aliquoted for analysis

9 4 1 If the sample will obviously yield no liquid when subjected to pressure filtration (i e is 100 % solid) aliquot 100 g (minimum) Transfer the aliquot to an appropriate extraction vessel (glass or plastic) and record the sample weight

If the sample is ≥ 0 5 % solids liquid/solid separation is required If enough solid sample was obtained from step 9 1 (determining the percent solids) then use the solid sample for the extraction and refrigerate the liquid portion at 4 °C If enough solid sample was not obtained from step 9 1 repeat step 9 1 using enough sample to generate enough solid sample Transfer the aliquot to an appropriate extraction vessel and record the weight of the solid sample (g equivalent solids)

If the sample is < 0 5 % solid the filtrate is the SPLP extract Filter enough sample to perform all analyses

9 4 2 Determine the amount of extraction fluid to add to the extractor vessel as follows

amount of extraction fluid to add in mL = 20 x weight of g equivalent solids of sample

Slowly add this amount of appropriate extraction fluid to the extraction vessel close the lid and secure in the rotation device

9 4 3 Rotate at 30 ± 2 rpm for 18 ± 2 hr The temperature of the room in which extraction takes place shall be maintained at 23 ± 2 °C during the extraction period Record the rpm of the rotation device the date and time the extraction started the date and time the extraction stopped and the minimum and maximum temperature during the extraction

NOTE As agitation continues pressure may build within the extractor bottle for some types of wastes (e g limed or calcium carbonate-containing waste may evolve gases such as carbon dioxide) To relieve excess pressure, the extractor bottle may be periodically opened (e g after 15 min, 30 min and 1 hr) and vented into a hood

9 4 4 Filter the material in the extractor vessel through a glass fiber filter into a glass container or plastic container if only metals are required For final filtration of the SPLP extract the glass fiber filter may be changed if necessary, to facilitate filtration

If the waste contained no initial liquid phase, the filtrate is defined as the SPLP extract

If the waste was multiphase and the previous filtered liquid phase is compatible with the filtrate (e g multiple phases will not result on combination) combine the liquid and filtrate to form the SPLP extract

If the initial liquid phase of the waste is not compatible with the filtrate analyze these liquids collectively defined as the SPLP extract and combine the results mathematically

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

9 4 5 Following the collection of the SPLP extract the pH of the extract should be recorded Immediately aliquot and preserve the extract for analysis Metals aliquots should be acidified with conc HNO_3 to pH < 2 If precipitation is observed upon addition of HNO_3 to the SPLP extract refrigerated the SPLP extract at 4 °C and analyze as soon as possible All other aliquots must be stored under refrigeration at 4 °C until analyzed The SPLP extract shall be prepared and analyzed according to appropriate analytical methods SPLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level then the waste is hazardous and digestion of the extract is not necessary However data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous If the individual phases are to be analyzed separately determine the volume of the individual phases (to ± 0 5 %) conduct the appropriate analyses and combine the results mathematically by using a simple volume-weighted average

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where
V1 = volume of the first phase (L)
C1 = concentration of the analyte of concern in the first phase (mg/L)
V2 = volume of the second phase (L)
C2 = concentration of the analyte of concern in the second phase (mg/L)

9 4 6 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations

9 5 Procedure when volatiles (VOA) are involved

Use the ZHE device to obtain SPLP extract for analysis of volatile compounds only Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e g metals pesticides, etc) Sample only once and do not open the device until the final extract (of the solid) has been collected as repeated filling of the ZHE to obtain 25 g of solid is not permitted Do not allow the waste the initial liquid phase or the extract to be exposed to the atmosphere for any more time than is absolutely necessary Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles

9 5 1 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid) Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample based upon sample size required Secure the gas inlet/outlet flange (bottom flange) onto the ZHE vessel Secure the glass fiber filter between (rough side of filter facing sample) the support screens and set aside Set the liquid inlet/outlet flange (top flange) aside

9 5 2 If the waste is 100 % solid aliquot a 25-g maximum transfer to the ZHE vessel and record the weight

If the waste is ≥ 0 5 % solids use the percent solids information to aliquot up to 25 g equivalent solids into the ZHE vessel and record the weight Waste slurries need not be allowed to stand to permit the solid phase to settle Do not centrifuge wastes prior to filtration

$$\text{mass of waste to charge filter (g)} = 25 \div \%\ \text{solids} \times 100$$

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

If the sample has a percent solids < 0 5 % the filtrate is the SPLP extract Fill the ZHE vessel with enough sample to filter to perform all the analyses
Transfer the entire sample (liquid and solid phases) quickly to the ZHE Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom)

NOTE If waste material (> 1 % of original sample mass) has obviously adhered to the container used to transfer the sample to the ZHE determine the mass of this residue and subtract it from the sample mass to determine the mass of the waste sample that will be extracted

9 5 3 Attach a gas line to the gas inlet/outlet valve (bottom flange) and with the liquid inlet/outlet valve (top flange) open begin applying gentle pressure up to 10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood

If the waste is 100 % solid, slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device

For a multiphase sample at the first appearance of liquid from the liquid inlet/outlet valve quickly close the valve and discontinue pressure If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering Attach the stainless steel syringe to the liquid inlet/outlet valve and open the valve Begin applying gentle pressure up to 10 psi to force the liquid phase of the sample into the filtrate collection container When no additional liquid has passed through the filter in a 2-min interval slowly increase the pressure in 10-psi increments to a maximum of 50 psi waiting at each 10-psi increment until a 2-min interval in which liquid does pass through the filter is reached When liquid flow has ceased for 2 min at 50 psi, stop the filtration Close the liquid inlet/outlet valve discontinue pressure to the piston disconnect and weigh the filtrate into a VOA vial The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase

NOTE Some wastes, such as oily wastes and some paint wastes will obviously contain some material that appears to be a liquid Even after applying pressure filtration, this material will not filter If this is the case, the material within the filtration device is defined as a solid and is carried through the SPLP extraction as a solid

The liquid phase may now be either analyzed immediately or stored at 4 °C under minimal headspace conditions until time of analysis

9 5 4 Determine the volume of extraction fluid #1 to add to the ZHE as follows

amount of extraction fluid to add in mL = 20 x weight of g equivalent solids of sample

Add the appropriate amount of extraction fluid to the ZHE vessel through the liquid inlet/outlet using a syringe or pump After the extraction fluid has been added immediately close the liquid inlet/outlet valve

9 5 5 Check the ZHE to ensure that all valves are in their closed positions Manually rotate the device in an end-over-end fashion 2 or 3 times Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top Pressurize the ZHE to 35 - 70 kPa (5-10 psi) In a hood slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid This bleeding shall be done quickly and shall be stopped at

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

the first appearance of liquid from the valve Re pressurize the ZHE with 35 - 70 kPa (5-10 psi) and check all ZHE fittings to ensure that they are closed

9 5 6 Place the ZHE in the rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hr Ambient temperature (i e temperature of room in which extraction occurs) shall be maintained at 22 ± 3 °C during agitation Record the time and temperature on the data sheets

9 5 7 Following the 18 ± 2 hr agitation period check the pressure of the ZHE If the pressure has not been maintained perform the extraction again with a new sample of waste If the pressure within the device has been maintained the extract is filtered through the glass fiber filter using the ZHE device as discussed in part 9 5 3

NOTE An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

NOTE All extract will be filtered

If the waste contained an initial liquid phase the extract is filtered into a separate filtrate collection container from the initial liquid phase of the waste The initial filtrate is identified as Z1 and the final filtered extract as Z2 Z1 and Z2 are collectively defined as the SPLP extract

If the original waste contained no initial liquid phase the ZHE filtrate defined as the SPLP extract

9 5 8 Following collection of the SPLP extract immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed Analyze the SPLP extract according to the appropriate analytical methods If the individual phases are to be analyzed separately (i e are not miscible) determine the volume of the individual phases (to 0 5%) conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where
V1 = volume of the first phase (L)
C1 = concentration of the analyte of concern in the first phase (mg/L)
V2 = volume of the second phase (L)
C2 = concentration of the analyte of concern in the second phase (mg/L)

9 5 9 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations

10 0 QUALITY CONTROL

10 1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel For samples that are < 0 5 % solids and are filtered only filter an equivalent amount of extraction fluid # 1 for use as a SPLP blank

10 2 A matrix spike shall be performed for each waste type (e g wastewater treatment sludge contaminated soil etc) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level A minimum of one matrix spike must be analyzed for each analytical batch Matrix spikes are to be added after filtration of the SPLP extract and before preservation In most cases matrix spikes should

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

be added at a concentration equivalent to the corresponding regulatory level (at a minimum of 5 × MDL) The purpose of the matrix spike is to monitor the performance of the analytical methods used and to determine whether matrix interferences exist The bias determined from the matrix spike determination shall **NOT** be used to correct the measured values

The % matrix spike (MS) recovery is calculated by the following formula

% MS recovery = ((spike result - sample result) ÷ spike added) × 100

10 3 All quality control measures described in the appropriate analytical methods shall be followed

10 4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if

(1) Recovery of the contaminant from the SPLP extract is not at least 50 % and the concentration does not exceed the regulatory level

and

(2) The concentration of the contaminant measured in the extract is within 20 % of the appropriate regulatory level

10 4 1 The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant

10 4 2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots The fourth aliquot is the unknown Preferably the first addition should be prepared so that the resulting concentration is approximately 50 % of the expected concentration of the sample The second and third additions should be prepared so that the concentrations are approximately 100 % and 150 % of the expected concentration of the sample All four aliquots are maintained at the same final volume by adding reagent water or a blank solution and may need dilution adjustment to maintain the signals in the linear range of the instrumental technique All four aliquots are analyzed

10 4 3 Subject data to linear regression of instrumental signals as the dependent variable (y-axis) versus concentrations of the additions of standard as the dependent variable (x-axis) Solve for the intercept of the abscissa (the independent variable x-axis) which is the concentration in the unknown

10 4 4 Alternately subtract the instrumental signal of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions Subject data to linear regression of the corrected instrument signals as the dependent variable versus the independent variable Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

10 5 Samples must undergo SPLP extraction within the following time periods

Sample Maximum Holding Times (days)

	From field collection to SPLP extraction	From SPLP extraction to preparative extraction	From preparative extraction to determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals except mercury	180	NA	180	360

If sample holding times are exceeded the values obtained will be considered minimal concentrations Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level

11 0 KEY WORDS

40 CFR 261 Method 1312 SW846 SPLP Synthetic Precipitation Leaching Procedure ZHE Zero Headspace Extraction

12 0 REFERENCES

12 1 USEPA, SW846 EPA Method-1312 Revised September 1994

12 2 Code of Federal Regulations 40 CFR 261 July 1992 revision 0

13 0 REVISION HISTORY

13 1 The method was updated on 06/01/09 to be more lab specific to reflect the current SOP format and to include additional safety information

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

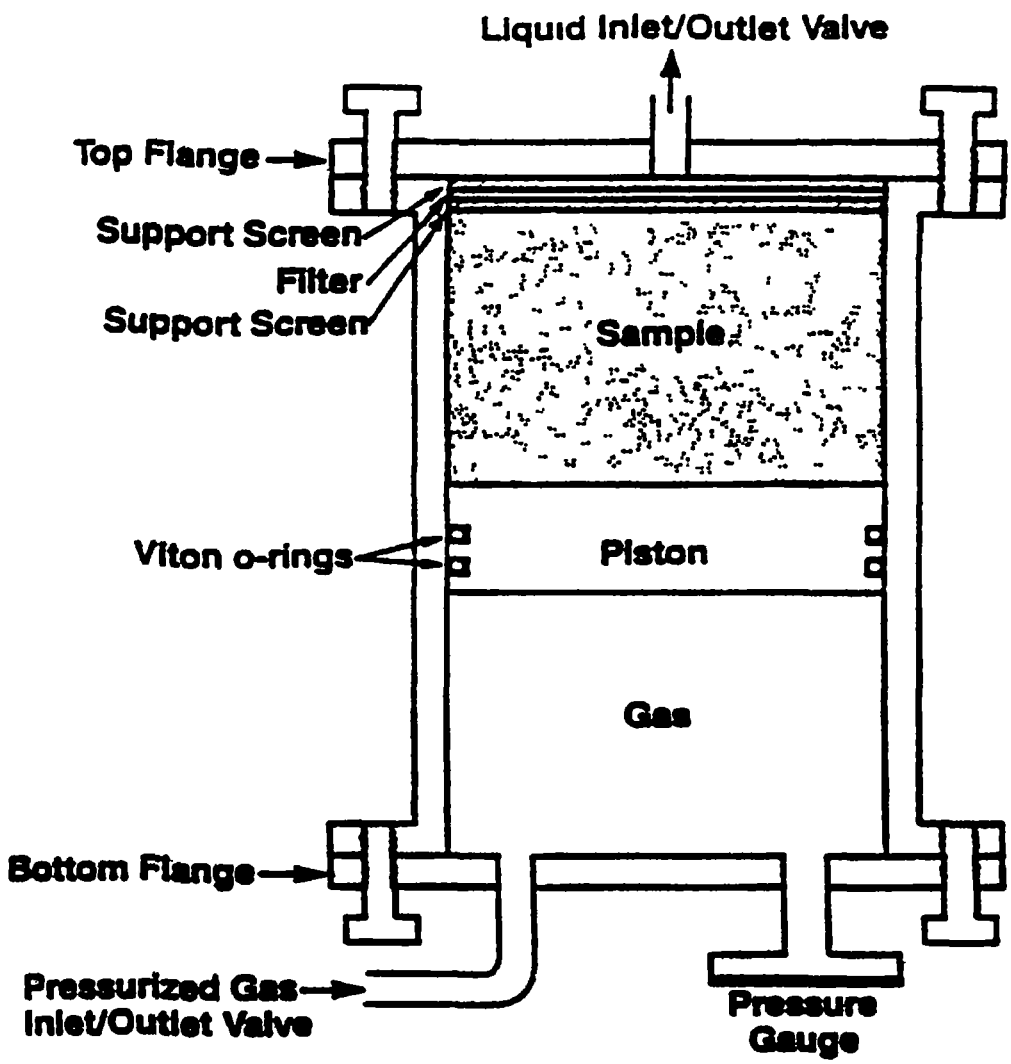


Figure 1 Zero-Headspace Extractor (ZHE)

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

TABLE 1
VOLATILE ANALYTES[1]

Compound	CAS No
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1 2-Dichloroethane	107-06-2
1 1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1 1 1-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1 1 2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1]When testing for any or all of these analytes the zero-headspace extractor vessel shall be used instead of the bottle extractor

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser

1 0 SCOPE

This method is used to calculate hardness in mg equivalent $CaCO_3$/L using calcium (Ca) and magnesium (Mg) results in mg/L This method is equivalent to Standard Methods 2340 B Hardness by Calculation (18th Edition, 1992)

2 0 SUMMARY OF METHOD

The concentration of calcium and magnesium in mg/L of a sample are determined using an ICP or ICPMS Hardness of the sample is calculated in mg equivalent $CaCO_3$/L

3 0 CALCULATION PROCEDURE

Hardness mg equivalent $CaCO_3$/L = 2 497 × [Ca mg/L] + 4 118 × [Mg, mg/L]

4 0 KEY WORDS

Ca, Calcium Hardness Calculation Magnesium Mg

5 0 REFERENCES

Standard Methods for the Examination of Water and Wastewater 18th Edition 1992 Method 2340 B

6 0 REVISION HISTORY

5/28/09-No changes needed