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RI/FS WORK PLAN

Four County Landfill Site
Fulton County, Indiana
Part II
Appendix H - Appendix J.

Prepared for:
The Four County Landfill Group

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APPENDIX H

SAMPLING AND ANALYSIS PLAN

APPENDIX H.1

FIELD SAMPLING AND ANALYSIS PLAN

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H.1.1.0 INTRODUCTION

The purpose of this Field Sampling and Analysis Plan (FSAP) is to outline the protocols to be implemented during the Remedial Investigation/Feasibility Study to be conducted at the Four County Landfill Site in Fulton County, Indiana (Site). This FSAP together with the Quality Assurance Project Plan (QAPP) provided in Section H.2.0 of this Appendix are intended to serve as the Sampling and Analysis Plan (SAP) for the RI/FS at the Site.

The FSAP presents general field protocols, sampling protocols, analytical protocols, project organization, objectives and specific quality assurance/quality control (QA/QC) activities associated with the RI/FS. The SAP provides a reference for personnel responsible for implementing and oversight of field activities during the performance of the RI/FS.

H.1.2.0 PROJECT DESCRIPTION

The Four County Landfill Site is located approximately one mile south of the Town of Delong in Fulton County, Indiana. History and background of the Site is presented in Sections 2.0 through 5.0 of this RI/FS Work Plan.

H.1.2.1 PROJECT OBJECTIVES

The overall objective of the RI/FS is to gather sufficient information to complete an evaluation of the nature and extent of contamination at this Site for purposes of assessing risk and ultimately selecting the most suitable Site remedy.

H.1.2.2 SCOPE OF WORK

The scope of work for field activities which will be performed during the RI are summarized below:

i) each of the existing Site monitoring wells and piezometers will be inspected;

ii) twenty-four existing monitoring wells and piezometers will be properly abandoned;

iii) groundwater samples will be collected from 71 existing monitoring wells and piezometers during the first investigative phase;

iv) sediment and surface water samples will be collected from 20 locations located both on- and off-Site;

v) hydraulic head data will be collected from the 71 monitoring wells and piezometers sampled during the RI;

vi) response tests will be performed at eight monitoring wells screened in the B and C stratigraphic units; and

vii) conduct additional characterization tasks, as required, after evaluation of the data compiled during the first phase.

All groundwater, surface water and sediment samples will be analyzed for contaminants which are likely to be present on the basis of historical data and information available for the Site. These compounds include the target compound list (TCL) volatile organic compounds (VOCs), TCL-semi-volatile organic compounds (SVOCs), target analyte list (TAL) metals and TAL cyanide. In addition to the above, groundwater samples will be analyzed for landfill indicator parameters such as hydrogen ion activity (pH), sulfate, chloride, nitrate, ammonia, total dissolved solid (TDS) total suspended solids (TDS) total suspended solids (TSS) and alkalinity. Sediment and surface water samples will also be analyzed for TCL pesticides and polychlorinated biphenyls (PCBs).

H.1.2.3 RATIONALE

The rationale for each of the field tasks to be performed during the RI are presented in Section 7.0 of this work plan. In general, sampling and analytical protocols have been selected to identify likely contaminants of concern on the basis of available historical information and data generated for the Site. Sampling locations have been selected to provide wide areal coverage over the landfilled property and the various stratigraphic units present beneath the Site (in the case of groundwater) and locations where contaminants may be present as a result of runoff and sediment deposition (surface water and sediments).

H.1.3.0 GENERAL PROTOCOLS

H.1.3.1 EQUIPMENT CLEANING

H.1.3.1.1 Drilling Equipment

Upon mobilization of the drill rig to the Site, and prior to commencing drilling, the rig and all associated equipment will be thoroughly steam cleaned to remove oil, grease, mud and other foreign matter. Before initiating drilling at each subsequent well abandonment location, the drill rods, cutting bits, samplers, hand auger, drill steel and associated equipment will be cleaned to prevent cross-contamination from the previous drilling. Cleaning will be accomplished by flushing and wiping the components to remove all visible sediments followed by:

i) steam clean or high pressure wash with tap water and Alconox™ detergent using a brush if necessary to remove particulate matter and surface films; and

ii) a thorough rinse with tap water.

H.1.3.1.2 Sampling Equipment

All sampling equipment will be decontaminated prior to field use and after each sample is collected to prevent cross-contamination between samples. Duplicate samples shall be collected concurrently with original samples; therefore, sampling equipment will not be decontaminated before collection of the duplicate. Decontamination of equipment will be performed as follows:

i) clean water and Alconox™ detergent wash using a brush, if necessary, to remove all visible foreign matter;

ii) rinse thoroughly with potable water;

iii) rinse with isopropyl alcohol;

iv) rinse thoroughly with deionized or distilled water;

v) allow the equipment to air dry on a clean plastic sheet as long as possible; and

vi) wrap in aluminum foil until ready to use.

Following final rinse, openings will be visually inspected to verify they are free of soil particulates and other solid material which may contribute to possible sample cross-contamination.

The Grundfos MP-1 or similar submersible pump and hose will be decontaminated between sampling locations using the following protocol:

i) The submersible pump and attached hose will be submerged in a suitably sized container which contains an Alconox and water solution.

ii) The outer casing of the submersible pump and the outer portion of the PVC hose will be cleaned using a brush to remove sediment or particulate matter. Upon completion of this procedure, the submersible pump will be started and detergent solution will be allowed to run through the pump and hose for a period of at least three minutes.

iii) The submersible pump and attached hose will then be placed in a suitably-sized container of potable water and turned on. Potable water will then be allowed to run through the pump and hose to flush out the detergent solution.

iv) The outer portion of the submersible pump will be rinsed with isopropyl alcohol.

v) The submersible pump will then be rinsed by submerging in deionized water and allowed to air dry as long as possible prior to use.

Fluids used for cleaning will not be recycled. All wash water, rinse water and decontamination fluids will be stored in containers on Site pending a review of potential disposal options.

H.1.3.2 FIELD SAMPLING

H.1.3.2.1 Sample Labelling

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. The sample numbering system is described below:

Example: GW-060191-WP-0001

GW	- designates type of sample (GW-groundwater, SW-surface water, D-sediment)
060191	- designates date of collection presented as month/day/year
WP	- sampler's initials
0001	- sequential number starting with 0001 at the start of the project

Quality Control (QC) samples also will be numbered with a unique sample number, consistent with the numbering system described above.

H.1.3.2.2 Field Log

The field log book will consist of a bound document with consecutively numbered pages. The entries for each day will commence on a new page which will be dated. Corrections will be made by marking through

the error with a single line, so as to remain legible, and initialing this action followed by writing the correction. The field log books generated will be numbered consecutively and maintained by Conestoga-Rovers & Associates (CRA) at the Rosemont, Illinois office.

The following information will be recorded in the field log book for each sample collected:

i) Site location identification;

ii) unique sample identification number;

iii) date and time (in military time format) of sample collection;

iv) weather conditions;

v) designation as to the type of sample (groundwater, sediment, etc.);

vi) designation as to the means of collection (grab, bailer, etc.);

vii) name of sampler;

viii) analyses to be performed on sample;

ix) personal protective equipment (PPE) worn during Site activities;

x) names of subcontractors and subcontractor personnel; and

xi) any other relevant comments such as odor, staining, texture, filtering, preservation, etc.

For the abandonment of monitoring wells, the following will be recorded in the field log book:

i) weather conditions;

ii) date of installation;

iii) type of drill rig used;

iv) length of time to abandon the well;

v) depth of well;

vi) well abandonment details; and

vii) subcontractor identity; and

viii) any other relevant comments.

Well purging details and the results of response tests on monitoring wells will be recorded on CRA standard forms, a copy of which will be kept in CRA's project files.

H.1.3.2.3 Chain-Of-Custody Records

CRA chain-of-custody records will be used to track all samples from time of sampling to the arrival of samples at the laboratory.

Each sample container being shipped to the laboratory will contain a chain-of-custody record. The chain-of-custody record consists of four copies which are distributed to the sampler, to the shipper, to the contract laboratory and to the office file of CRA. The sampler and shipper will maintain their copies while the other two copies are placed in a waterproof enclosure within the sample container. The laboratory, upon receiving the samples, will complete the remaining copies. The laboratory will maintain one copy for its records. The executed original will be returned to CRA with the data deliverables package. A typical chain-of-custody record is presented on Figure H.1.1.

CRA
CONESTOGA-ROVERS & ASSOCIATES
10400 West Higgins Road - Suite 103
Rosemont, IL 60018 (708)299-9933

CHAIN OF CUSTODY RECORD

SHIPPED TO (Laboratory Name):

REFERENCE NUMBER: | PROJECT NAME:

SAMPLER'S SIGNATURE: | PRINTED NAME:

SAMPLE

SEQ. No.	DATE	TIME	SAMPLE No.	SAMPLE MATRIX	No. OF CONTAINERS	PARAMETERS										REMARKS
			TOTAL NUMBER OF CONTAINERS													

RELINQUISHED BY: ①	DATE: TIME:	RECEIVED BY: ②	DATE: TIME:
RELINQUISHED BY: ②	DATE: TIME:	RECEIVED BY: ③	DATE: TIME:
RELINQUISHED BY: ③	DATE: TIME:	RECEIVED BY: ④	DATE: TIME:
METHOD OF SHIPMENT:		AIR BILL No.	

White -Fully Executed Copy Yellow -Receiving Laboratory Copy Pink -Shipper Copy Goldenrod -Sampler Copy	SAMPLE TEAM:	RECEIVED FOR LABORATORY BY: DATE: TIME:

figure H.1.1

CHAIN-OF-CUSTODY RECORD
FOUR COUNTY LANDFILL SITE
Fulton County, Indiana

CRA

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H.1.3.2.4 Sample Containers and Handling

Required sample containers, sample preservation methods, maximum holding times and filling instructions are provided in Table H.1.1 and the QAPP in Appendix H.2.

All samples will be placed in appropriate sample containers, labeled and properly sealed. The sample labels will include sample number, place of collection, date and time of collection and analyses to be performed. Samples will be cushioned within the shipping coolers by the use of vermiculite, foam chips and/or bubble pack. Samples will be kept cool by the use of sealed plastic bags of ice or cooler packs. A trip blank will accompany each shipment of groundwater samples submitted for VOC analysis.

Samples will be shipped by commercial courier on a daily basis to the project laboratory. The exception to this will be samples which are collected on a Sunday or holiday. For samples collected on a Sunday or holiday, additional ice will be placed in the coolers, the coolers will be sealed and kept under surveillance, and picked up by the courier on the next business day.

Two seals comprised of CRA chain-of-custody tape will be placed over the lid on the front and back of each shipping cooler prior to shipment to secure the lid and provide evidence that the samples have not been tampered with en route to the laboratory. Clear tape will be placed over the seals to ensure that they are not accidentally broken during shipment.

Upon receipt of the cooler at the laboratory, the cooler will be inspected by the designated sample custodian. The condition of the cooler and seal will be noted on the chain-of-custody record by the sample custodian.

The sample custodian then will check the contents of the cooler with those samples listed on the chain-of-custody record. If damage or discrepancies are noticed, they will be recorded in the remarks column of the

TABLE H.1.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Analyses	*Sample Containers*	*Preservation*	*Maximum Holding Time from Sample Collection**	*Volume of Sample*	*Shipping*	*Normal Packaging*
Groundwater						
TCDD	Two 1-liter amber glass bottles	Iced, 4 °C	30 days for extraction 45 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL SVOC, Appendix IX SVOC, Appendix IX Pest/PCB, Appendix IX Herbicides	Two 1-liter amber glass bottles per analysis	Iced, 4° C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL VOC, Appendix IX VOC	Three 40-mL teflon lined septum vials per analysis	HCl to pH <2, Iced, 4 °C	14 days for analysis	Fill completely, no air bubbles	Federal Express Priority 1	Foam Liner
TAL Total Metals, TAL Dissolved Metals, Appendix IX Metals	One 1-liter plastic bottle per analysis	HNO3 to pH <2, Iced, 4 °C	6 months (mercury - 28 days) for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Cyanide	One 1-liter plastic bottle	NaOH to pH >12, Iced, 4 °C	14 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
BOD	One 1-liter polyethylene	Iced, 4 °C	48 hours to incubation	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Total Suspended Solids, Total Dissolved Solids	One 1-liter polyethylene	Iced, 4 °C	7 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Alkalinity, Chloride, Sulfate	One 1-liter polyethylene	Iced, 4 °C	28 days (Alkalinity 14 days) for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips

TABLE H.1.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Analyses	*Sample Containers*	*Preservation*	*Maximum Holding Time from Sample Collection**	*Volume of Sample*	*Shipping*	*Normal Packaging*
Ammonia, Nitrate, COD	One 1-liter polyethylene	H2SO4 to pH<2 Iced, 4 °C	28 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Sediment						
TCL SVOC, TCL Pesticides/PCB	One 8-ounce glass per analysis	Iced, 4 °C	14 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL VOC	One 4-ounce glass	Iced, 4 °C	14 days for analysis	Fill completely	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Metals	One 16-ounce glass	Iced, 4 °C	6 months (mercury - 28 days) for analysis	Fill to shoulder of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Cyanide	No additional jar necessary	Iced, 4 °C	14 days for analysis	Fill to shoulder of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Surface Water						
TCL SVOC, TCL Pesticides/PCB	Two 1-liter amber glass bottles per analysis	Iced, 4 °C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL VOC	Three 40-mL teflon lined septum vials	HCl to pH <2, Iced, 4 °C	14 days for analysis	Fill completely, no air bubbles	Federal Express Priority 1	Foam Liner
TAL Metals	One 1-liter plastic bottle	HNO3 to pH <2, Iced, 4 °C	6 months (mercury - 28 days) for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Cyanide	One 1-liter plastic bottle	NaOH to pH >12, Iced, 4 °C	14 days for analysis	Fill to neck of bottle	Federal Express	Bubble Wrap or Foam Chips

* - These are technical holding times; (i.e., are based on time elapsed from time of sample collection).

chain-of-custody record, dated and signed. They will be reported to the laboratory supervisor who will inform the laboratory project manager and QC officer.

H.1.4.0 FIELD PROTOCOLS

In order to meet the objectives of the RI/FS at the Four County Landfill Site, the following field activities will be implemented:

i) inspection of all accessible existing Site monitoring wells;

ii) collection of groundwater samples for chemical analysis from 71 existing Site monitoring wells and piezometers;

iii) abandonment of 24 existing Site monitoring wells with excessively long effective screen lengths and improper construction specifications;

iv) collection of on- and off-Site sediment and surface water samples for chemical analysis; and

v) collection of hydraulic head and response test data.

Sediment, surface water and groundwater sampling protocols are discussed in Section H.1.5.0. Protocols for general field tasks are discussed below. Monitoring well locations are provided in Figure H.1.2.

H.1.4.1 MONITORING WELL AND PIEZOMETER INSPECTION

A large number of monitoring wells and piezometers (approximately 118) are known to have been installed at the Site. Therefore, prior to initiation of monitoring well/piezometer abandonment activities, a thorough inventory and inspection of all existing Site monitoring wells and piezometers will be conducted. Each Site monitoring well/piezometer will be carefully inspected and the information recorded on the standard CRA monitoring well inspection checklist.

The identity of each monitoring well/piezometer will be confirmed by comparing data recorded during the inspection with available

SOUTHWEST QUADRANT WEST QUADRANT

1+00E

2+00E

3+00E

4+00E

5+00E

6+00E

7+00E

8+00E

9+00E

10+00E

11+00E

12+00E

13+00E

SOUTHEAST QUADRANT EAST QUADRANT

0 100 200ft

SOURCE:
MODIFICATION OF A SITE MAP (4/15/91)
OBTAINED FROM
GEOSCIENCES RESEARCH
ASSOCIATES, INC.

LEGEND

165	BLOCK NUMBERS OF GRID
• P-30C1	PIEZOMETERS
• B-25R	BORINGS
• 22	MONITORING WELLS
—×—×—	FENCE LINE

NOTE
SITE GRID = 100 FEET.

figure H.1.2

MONITORING WELL LOCATIONS
FOUR COUNTY LANDFILL SITE
Fulton County, Indiana

CRA

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well records, Site maps, and identification marks present. Monitoring wells and piezometers slated for abandonment will be marked with flagging tape.

On the basis of the detailed field inspection, additional monitoring wells and piezometers may be identified for abandonment. Recommendations and justifications for abandonment of additional monitoring wells will be presented to IDEM. IDEM will be contacted for approval to abandon additional monitoring wells or piezometers. Specific situations which may occur that may result in a monitoring well or piezometer being identified for abandonment include:

i) depth measurements which vary considerably from data recorded in well logs that may indicate damage or plugging of the well/piezometer; and

ii) damaged casings which may compromise the integrity or prevent collection of a groundwater sample from a well/piezometer.

Should these or other situations occur which prevent the collection of, or compromise the integrity of groundwater samples from a specific monitoring well or piezometer, this situation will be documented by CRA. IDEM will be contacted regarding the specifics of this situation and CRA's recommendation for abandonment. Appropriate action will then be initiated following this discussion. A summary of monitoring well and piezometer construction data is presented on Table H.1.2.

H.1.4.2 MONITORING WELL/PIEZOMETER ABANDONMENTS

Monitoring wells and piezometers with excessively long effective screen lengths, inappropriate construction specifications, or providing redundant monitoring of a specific stratigraphic unit will be properly abandoned to minimize cross-contamination between geologic units. Table H.1.3 provides a summary of monitoring wells and piezometers which will be abandoned.

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Piezometer/ Well ID	*Stratigraphic Unit(s) Screened*	*Former/ Other ID* [2]	*Casing Elevation (feet amsl)*	*Site Quadrant* [3]	*Date of Installation*	*Well Depth (feet bgs)/ Bottom Elevation (feet amsl)*	*Screen Length (feet)*	*Sand Pack Length (feet)*	*Well Construction Details* [4]	*Comments*
P-1	B	MW-1B	783.07	SW	12/08/86	65.0/718.1	5	13.0	hand slotted PVC, 1" dia., 3.75" dia. borehole,	
P-1A	A	--	787.64	SW	12/05/88	37.1/749.2	2	2.7	4.25" dia. borehole, 2' bentonite seal, [5]	
P-2	B	--	777.55	SW	12/15/86	80.0/697.9	10	12.0	hand slotted PVC, 1" dia., 7.25" dia. borehole, 8' bentonite seal	
P-2A	A	--	777.38	SW	12/05/88	17.0/758.0	2	2.6	4.25" dia. borehole, 3' bentonite seal, [5]	
P-2B	B	MW-2B	777.05	SW	12/05/88	72.2/702.7	4	6.4	4.25" dia. borehole, 7.8' bentonite seal, [5]	
P-2C2	C	--	776.86	SW	12/09/89	134.9/639.8	2	5.5	4.9" dia. borehole, no bentonite seal, [5]	
P-3	B?	--	772.71	SW	12/10/86	50.9/715.4	5	18.9	hand slotted PVC, 1" dia., 3.75" dia. borehole, 2' bentonite seal	Assume casing removed 12/19/86.
P-3A	A?	--	766.22	SE	unknown	unknown	unknown	unknown	unknown	Assume casing removed during Cell B construction.
P-4A	A	--	790.03	SE	11/07/88	19.0/769.1	2	2.8	4.25" dia. borehole, 2' bentonite seal, [5]	
P-4B	B	--	790.00	SE	11/04/88	69.6/718.6	2	6.4	4.25" dia. borehole, 2.7' bentonite seal, [5]	
P-4C1	C	--	791.02	SE	01/04/89	85.6/703.9	2	4.0	4.9" dia. borehole, no bentonite seal, [5]	
P-4C2	C	--	791.72	SE	01/03/89	132.9/656.7	2	4.0	4.9" dia. borehole, no bentonite seal, [5]	
P-4C3	C	--	791.71	SE	02/02/89	155.6/633.9	2	4.5	4.9" dia. borehole, no bentonite seal, [5]	
P-4C4	C	--	791.02	SE	01/27/89	152.5/637.0	2	4.0	Schedule 80 PVC, 4.9"dia. borehole, no bentonite seal, [5]	
P-5A	A/B?	--	776.93	SW	11/08/88	28.1/746.3	2	4?	4.25" dia. borehole, 2' bentonite seal, [5]	
P-5B	B	MW-5B	776.86	SW	11/03/88	49.1/725.0	2	6.1	4.25" dia. borehole, 2' bentonite seal, [5]	
P-5C1	C	--	776.63	SW	01/12/89	77.1/696.6	2	3.0	4.5" dia. borehole, no bentonite seal, [5]	
P-5C2	C	--	777.29	SW	01/18/89	107.4/666.9	2	4.0	4.9" dia. borehole, 2' bentonite seal, [5]	
P-5C3	C	--	777.05	SW	01/18/89	119.8/654.5	2	2.8	4.25" dia. borehole, 2' bentonite seal, [5]	
P-5C4	C	--	777.23	SW	01/29/89	166.2/608.3	2	5.0	Schedule 80 PVC, 4.9"dia. borehole, no bentonite seal, [5]	

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Piezometer/ Well ID	*Stratigraphic Unit(s) Screened*	*Former/ Other ID* [2]	*Casing Elevation (feet amsl)*	*Site Quadrant* [3]	*Date of Installation*	*Well Depth (feet bgs)/ Bottom Elevation (feet amsl)*	*Screen Length (feet)*	*Sand Pack Length (feet)*	*Well Construction Details* [4]	*Comments*
P-6A	A		776.57	SW	11/01/88	21.0/752.9	2	3.0	4.25" dia. borehole, 2.1' bentonite seal, [6]	
P-7A	B	--	771.24	NE	11/18/88	21.4/748.0	2	2.7	4.25" dia. borehole, 2' bentonite seal, [5]	
P-7B	B	MW-7B	770.92	NE	11/17/88	50.9/718.4	5	6.0	4.25" dia. borehole, 2' bentonite seal, [5]	
P8A	A	--	757.70	NE	11/23/88	19.9/735.4	2	3.9	4.25" dia. borehole, 2' bentonite seal, [5]	
P-8B	B	MW-8B	756.99	NE	11/02/88	47.9/707.2	4	5.5	4.25" dia. borehole, 6' bentonite seal, [5]	
P-8C1	C	--	757.71	NE	01/25/89	79.8/675.3	2	3.8	5.25" dia. borehole, no bentonite seal, [5]	
P-8C2	C	--	757.68	NE	01/27/89	113.0/642.8	2	4.0	4" dia. borehole, no bentonite seal, [5]	
P-8C3	C	--	757.34	NE	01/26/89	133.5/622.1	2	4.5	4.75" dia. borehole, no bentonite seal, [5]	
P-8C4	C	MW-8C4	757.68	NE	01/03/89	180.5/575.3	2	5.4	Schedule 80 PVC, 5.75" dia. borehole, no bentonite seal, [5]	
P-10	A	P-10A	797.05	NW	11/18/88	14.5/779.4	2	2.8	4.25" dia. borehole, 2' bentonite seal, [5]	Drilled through refuse
P-11A	A	--	796.20	NW	11/21/88	13.5/780.6	2	3.2	4.25" dia. borehole, 2' bentonite seal, [5]	
P-12A	A	--	796.90	NW	11/16/89	19.6/774.2	2	3.0	3.25" dia. borehole, 0.5' bentonite seal, [5]	Drilled through refuse
P-13A	A	--	799.94	NW	11/17/89	21.6/775.2	4	6.0	3.25" dia. borehole, 1' bentonite seal, screened in refuse.[5]	Drilled through refuse
P-14A	A	--	797.72	NW	11/20/89	21.5/773.2	4	5.5	3.25" dia. borehole, 1' bentonite seal, [5]	Drilled through refuse
P-21A	A	MW-21A	776.50	SE	11/09/88	22.3/752.2	2	2.8	4.25" dia. borehole, 2' bentonite seal, [5]	
P-23A	A	MW-23A	760.15	NE	11/23/88	19.3/738.5	2	3.3	4.25" dia. borehole, 2' bentonite seal, [5]	
P-23C1	C	--	761.08	NE	01/13/89	77.7/680.4	2	5.9	4.75" dia. borehole, no bentonite seal, [5]	
P-23C2	C	--	761.15	NE	01/12/89	116.1/642.0	2	3.7	4.75" dia. borehole, no bentonite seal, [5]	
P-23C3	C	--	760.83	NE	01/12/89	136.5/621.1	2	3.9	4.75" dia. borehole, no bentonite seal, [5]	
P-23C4	C	--	760.03	NE	01/18/89	177.7/580.5	2	4.5	Schedule 80 PVC, 5.75" dia. borehole, no bentonite seal, [5]	Two points identified on 4/15/91 site map
P-24A	A	MW-24A	788.29	SW	12/04/88	28.8/757.5	2	2.7	4.25" dia. borehole, 2' bentonite seal, [5]	
P-24AC1	C	--	788.32	SW	01/19/89	89.9/696.2	2	4.4	4.75" dia. borehole, no bentonite seal, [5]	
P-24C2	C	--	787.90	SW	01/18/89	104.9/681.2	2	3.2	4.75" dia. borehole, no bentonite seal, [5]	
P-24C3	C	--	788.51	SW	01/17/89	119.1/666.9	2	4.5	4.75" dia. borehole, no bentonite seal, [5]	
P-24C4	C	--	788.43	SW	01/16/89	131.2/654.9	2	4.4	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, [5]	

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Piezometer/ Well ID	*Stratigraphic Unit(s) Screened*	*Former/ Other ID* [2]	*Casing Elevation (feet amsl)*	*Site Quadrant* [3]	*Date of Installation*	*Well Depth (feet bgs)/ Bottom Elevation (feet amsl)*	*Screen Length (feet)*	*Sand Pack Length (feet)*	*Well Construction Details* [4]	*Comments*
P-25A	A	MW-25A	793.83	SE	12/06/88	32.2/759.9	2	3.0	4.25" dia. borehole, 2.3' bentonite seal, [5]	
P-25C2	C	--	794.86	SE	01/20/89	122.0/670.4	2	4.0	4.75" dia. borehole, no bentonite seal, [5]	
P-26A	A	--	792.32	NW	11/21/89	13.9/775.3	3.5	3.7	3.25" dia. borehole, 0.5' bentonite seal, [5]	
P-27A	A	MW-27A	780.32	SE	12/01/88	17.0/761.6	2	3.5	4.25" dia. borehole, 2' bentonite seal, [5]	
P-27C1	C	--	780.42	SE	01/13/89	79.3/699.8	2	4.0	4.75" dia. borehole, no bentonite seal, [5]	
P-27C2	C	--	780.10	SE	01/10/89	109.3/669.4	2	5.0	4" dia. borehole, no bentonite seal, [5]	
P-27C3	C	--	780.10	SE	01/12/89	130.3/648.4	2	6.0	4.25" dia. borehole, no bentonite seal, [5]	
P-27C4	C	--	781.96	SE	01/17/89	18.7/599.5	2	4.5	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, [5]	
P-28A	A	MW-28A	775.37	NE	11/28/88	26.1/748.2	2	3.0	4.25" dia. borehole, 2' bentonite seal, [5]	
P-28C1	CB	--	777.05	NE	01/16/89	85.0/689.4	2	3.2	4.25" dia. borehole, no bentonite seal, [5]	
P-28C2	C	--	776.35	NE	01/26/89	121.9/652.2	2	4.5	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, [5]	
P-28C3	C	--	776.79	NE	01/26/89	135.1/639.1	2	6.0	4.75" dia. borehole, no bentonite seal, [5]	
P-28C4	C	--	776.50	NE	01/25/89	201.8/572.3	2	7.0	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, [5]	
P-29A	A	MW-29A	773.78	NE	11/30/88	13.5/758.1	2	2.4	4.25" dia. borehole, 4' bentonite seal, [5]	
P-29C2	C	--	772.92	NE	01/18/89	116.2/655.4	2	4.9	4" dia. borehole, no bentonite seal, [5]	
P-30A	A	MW-30A	761.97	NW	11/22/88	20.4/739.6	2	2.9	4.25" dia. borehole, 2.5' bentonite seal, [5]	
P-30C1	C	--	762.56	NW	01/23/89	59.8/700.0	2	4.3	4" dia. borehole, no bentonite seal, [5]	
P-30C2	C	--	764.02	NW	01/31/89	102.4/659.2	2	4.5	4.75" dia. borehole, no bentonite seal, [5]	
P-30C3	C	--	764.37	NW	01/30/89	122.4/639.1	2	4.2	4.75" dia. borehole, no bentonite seal, [5]	
P-30C4	C	--	762.87	NW	01/19/89	219.8/541.0	2	10.3	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, (5)	

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Piezometer/ Well ID	*Stratigraphic Unit(s) Screened*	*Former/ Other ID* [2]	*Casing Elevation (feet amsl)*	*Site Quadrant* [3]	*Date of Installation*	*Well Depth (feet bgs)/ Bottom Elevation (feet amsl)*	*Screen Length (feet)*	*Sand Pack Length (feet)*	*Well Construction Details* [4]	*Comments*
P-31A	A	MW-31A	783.02	NW	11/29/88	14.9/765.7	2	2.9	4.25" dia. borehole, 2' bentonite seal, [5]	
P-31C1	C	--	782.78	NW	01/10/89	86.7/694.0	2	2.6	4.75" dia. borehole, no bentonite seal, [5]	
P-31C2	C	--	782.60	NW	01/09/89	111.6/669.1	2	2.5	4.75" dia. borehole, no bentonite seal, [5]	
P-31C3	C	--	782.75	NW	01/06/89	134.2/646.5	2	3.5	4" dia. borehole, no bentonite seal, [5]	
P-31C4	C	--	782.77	NW	01/17/89	194.1/586.5	2	3.4	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, [5]	
P-32A	A	--	798.53	NW	11/22/89	18.1/777.7	4.5	5.0	3.25" dia. borehole, 0.3' bentonite seal, [5]	
P-32C2	C	--	797.84	NW	01/13/89	130.8/665.0	2	2.8	4.75" dia. borehole, no bentonite seal, [5]	
P-33A	A	MW-33A	798.06	NW	11/11/88	20.0/775.2	2	3.1	4.25" dia. borehole, 2' bentonite seal, [5]	
P-34A	A	MW-34A	794.73	NW	10/11/88	18.8/772.8	2	2.7	4.25" dia. borehole, 2' bentonite seal, [5]	Drilled through refuse. Removed 11/07/89. Now a sump.
P-34*A	A	MW-34*A	796.01	NW	12/07/88	26.0/767.9	1.3	3.0	4.25" dia. borehole,2' bentonite seal, [5]	
P-34*C1	C	--	796.16	NW	01/10/89	97.7/696.4	2	2.7	4.25" dia. borehole, no bentonite seal, [5]	
P-34*C2	C	--	795.88	NW	01/12/89	126.6/667.3	2	4.0	4.75" dia. borehole, no bentonite seal, [5]	
P-34*C3	C	--	796.27	NW	01/11/89	149.8/644.1	2	3.8	4.75" dia. borehole, no bentonite seal, [5]	
P-34*C4	C	--	796.29	NW	01/11/89	193.7/600.3	2	3.7	Schedule 80 PVC, 4.75" dia. borehole, no bentonite seal, [5]	
MW-1	A/B?	W-1	790.61	NW	12/26/78	42/749	2	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	Buried?
MW-2	A	W-2	769.88	NE	12/26/78	20/750	2	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	Not accessible ?
MW-3	A?	W-3	771.57	NE	12/27/78	38/732	2	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	
MW-4	A	W-4	786.24	SE	02/20/79	19/?	7?	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	Disturbed, casing broken.

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Piezometer/ Well ID	*Stratigraphic Unit(s) Screened*	*Former/ Other ID* [2]	*Casing Elevation (feet amsl)*	*Site Quadrant* [3]	*Date of Installation*	*Well Depth (feet bgs)/ Bottom Elevation (feet amsl)*	*Screen Length (feet)*	*Sand Pack Length (feet)*	*Well Construction Details* [4]	*Comments*
MW-5	B	W-5	789.23	SE	02/20/79	35/740	2	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	
MW-6	A/B?	W-6	780.63	SW	01/03/79	51/724	2	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	Formerly buried. Casing raised ~3.5
MW-7	B?	W-7	776.87	SW	12/29/78	36/737	2	unknown	4" dia. casing, glued joints, 25-slot screen, no bentonite seal or grout	Not accessible. Buried?
MW-8	B/C?	W-8	unknown	NW	unknown	unknown	unknown	unknown	unknown	Former residential well. Buried?
MW-20	A/B?	W-20	767.23	NE	05/19/83	45.5/721.7	15	17.5	4" dia. PVC, 10.5" dia. borehole, 2' bentonite seal	Possible grout contamination.
MW-21S	B	W-21, MW021	778.00	SE	05/27/83	60.0/718.0	15	20.0	4" dia. PVC, 10.5" dia. borehole, 2' bentonite seal	
MW-21M	C	--	777.37	SE	01/27/87	94.8/682.5	10	18.3	4.25" dia. borehole, 11.5' bentonite seal	
MW-21L	C	--	777.01	SE	01/20/87	212.0/565.0	10	14.0	4.25" dia. borehole, 5' bentonite seal	
MW-22	B	--	757.17	NW	06/01/83	38.5/718.7	15	14.5	4" dia. PVC, 10.5" dia. borehole, 2' bentonite seal	
MW-23B	B	MW-23BW	759.84	NE	11/22/88	39.4/718.2	5	7.0	4.5" dia. borehole, 2' bentonite seal	
MW-23S	A/B	--	765.41	NE	04/08/85	48.0/717.4	20	24.0	6.5" dia. borehole	
MW-23M	A/B/C	--	765.46	NE	04/08/85	85.5/680.0	20	69.5	6.5" dia. borehole, 1' bentonite seal	
MW-23L	B/C	MW-23D	765.50	NE	04/08/85	122.0/643.5	20	92.0	6.5" dia. borehole, 1' bentonite seal	
MW-24B	B	P-24B	787.70	SW	12/04/88	74.2/711.9	5	7.0	4.5" dia. borehole, 2' bentonite seal [5]	
MW-24S	C	P-24S	789.66	SW	12/05/86	75.0/714.7	10	19.0	7.25" dia. borehole, 5' bentonite seal	
MW-24M	B/C	P-24M	788.96	SW	01/26/87	108.5/680.5	10	28.5	4.5" dia. borehole, 5' bentonite seal	

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Piezometer/ Well ID	*Stratigraphic Unit(s) Screened*	*Former/ Other ID* [2]	*Casing Elevation (feet amsl)*	*Site Quadrant* [3]	*Date of Installation*	*Well Depth (feet bgs)/ Bottom Elevation (feet amsl)*	*Screen Length (feet)*	*Sand Pack Length (feet)*	*Well Construction Details* [4]	*Comments*
MW-24L	C/D	MW-24L1, P-24L	788.86	SW	01/22/87	142.8/646.0	10	22.8	4.5" dia. borehole, 5' bentonite seal	Abandoned, not plugged. High pH-grout? Replaced.
MW-24L2	C	MW-24L1, P-24L2	788.65	SW	4/87, 5/87	136.0/652.6	10	36.0	Schedule 80 PVC, 4.5" dia. borehole, 56' bentonite seal	
MW-25	A/B	OW-25	789.96	SE	12/17/86	74.0/716.0	10	38.0	7.25" dia. borehole, 5' bentonite seal	Possible grout contamination.
MW-25B	B/C?	MW-25BW,	793.81	SE	12/07/88	78.5/713.7	5	6.5	4.5" dia. borehole, 2' bentonite seal, [5]	
MW-26	B	OW-26	791.40	NW	01/06/87	77.2/14.2	10	16.7	4.5" dia. borehole, 5.5' bentonite seal [5]	
MW-27B	B	MW-27BW	779.76	SE	12/01/88	55.0/723.2	5	7.0	4.25" dia. borehole, 2.5' bentonite seal, [5]	
MW-27S	B/C	--	778.95	SE	04/29/87	72.0/707.0	10	34.0	4.5" dia. borehole, 9.3' bentonite seal, [5]	
MW-27M	B/C	--	779.44	SE	04/29/87	101.4/678.0	5	48.4	4.5" dia. borehole, 10' bentonite seal, [5]	
MW-28B	B	MW-28BW	775.64	NE	11/28/88	60.0/713.7	10	6.8	4.25" dia. borehole, 2' bentonite seal, [5]	
MW-28S	A/B	--	775.71	NE	05/04/87	60.5/715.2	5	17.5	4.5" dia. borehole, 10' bentonite seal, [5]	
MW-28M	B/C	--	776.20	NE	05/01/87	101.1/675.2	10	28.0	4.5" dia. borehole, 5' bentonite seal, [5]	
MW-29B	B	MW-29BW	773.43	NE	11/30/88	51.9/719.3	10	7.4	4.25" dia. borehole, 9.8' bentonite seal, [5]	
MW-30B	B	MW-30BW	462.02	NW	11/21/88	42.2/718.8	5	8.2	4.25" dia. borehole, 4' bentonite seal, [5]	
MW-31B	B	MW-31BW	782.99	NW	11/29/88	61.9/719.0	5	6.9	4.5" dia. borehole, 3' bentonite seal, [5]	
MW-32B	B	P-32B,	798.89	NW	11/14/88	78.0/718.4	5	8.0	4.5" dia. borehole, 2' bentonite seal, [5]	
MW-33B	B	MW-33BW	796.57	NW	11/10/88	725./722.2	5	8.5	4.25" dia. borehole, 12' bentonite seal, [5]	
MW-34*B	B	MW-34B	796.15	NW	12/06/88	74.9/719.2	4.2	6.2	4.25" dia. borehole, 2' bentonite seal, [5]	
6" Diameter Supply Well	B/C?	unknown	796.78	NW	unknown	unknown	unknown	unknown	unknown	
Former Support Facilities (Trailer Well)	unknown	unknown	unknown	SE	unknown	unknown	unknown	unknown	unknown	

TABLE H.1.2

SUMMARY OF MONITORING WELL AND PIEZOMETER DATA[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

[1] This monitoring well and piezometer summary was derived from data tables and well construction logs included in the following sources:

- Site Map (4/15/91) obtained from Geosciences Research Associates, Inc.;
- "CAP Task I - Description of Current Conditions", Geosciences Research Associates, Inc. (12/7/89);
- Memorandum Report, Geosciences Research Associates, Inc. (4/28/89); and
- "Hazardous Waste Groundwater Task Force Evaluation of the Four County Landfill, Fulton County, IN", USEPA, May 1987.

[2] Stratigraphic units are defined as follows:

A = Glacial till sequence, silty clay loam with silt and sand seams;
B = Glacio-lacustrine sequence, silt to fine- to medium-grained sand;
C = Glacio fluvial sequence, poorly sorted silt, sand, and gravel; and
D = Basal till, silty clay with reddish hue at base.

[3] Site quadrants are arbitrarily defined by the 7+00 North and 8+00 East survey grid lines.

[4] Well materials are assumed to be 2-inch diameter, threaded, Schedule 40 PVC with a 10-slot screen, unless otherwise noted.

[5] Well annulus filled with Volclay grout from filter pack or annular seal to surface.

[6] Well annulus filled with pea gravel and bentonite grout from filter pack or annular seal to surface.

Key:

amsl = Above mean sea level
bgs = Below ground surface
dia. = Diameter
unknown = Information incomplete or unavailable
– = Not applicable

TABLE H.1.3

GROUNDWATER MONITORING WELLS AND PIEZOMETERS TO BE ABANDONED FOUR COUNTY LANDFILL SITE FULTON COUNTY, INDIANA

Northwest Quadrant	*Northeast Quadrant*
MW-1	MW-2
MW-8	MW-3
MW-22	MW-20
	MW-23S
	MW-23M
	MW-23L
	MW-28S
	MW-28M
Total = 3	Total = 8

Southwest Quadrant	*Southeast Quadrant*
MW-6	MW-4
MW-7	MW-5
MW-24S	MW-25
MW-24M	MW-27S
MW-24L	MW-27M
MW-24L2	P-4C4
P-2	
P-5A	
Total = 7	Total = 6

Total - All Quadrants = 24

Abandonments will be accomplished using the following procedure:

i) The protective casing and cement pads will be removed from the ground and the diameter of the well casing will be noted.

ii) The well cap will be removed and the breathing zone will be monitored with a photoionization detector, combustible gas meter, a hydrogen cyanide meter and a hydrogen sulfide meter.

iii) The monitoring well/piezometer will be overdrilled using a 6-inch nominal diameter (2-inch or smaller diameter wells) or an 8-inch nominal diameter (4-inch diameter wells) tricone roller bit and mud rotary drilling methods. The drilling fluid will consist of Volclay or equivalent and mixed to a minimum density of 9.4 pounds per gallon.

iv) Upon reaching a depth of one foot below the measured total depth of the well, borehole advancement will cease and drilling rods will be removed from the borehole.

v) A tremie pipe will then be lowered into the borehole and a bentonite grout mixture will be pumped into the borehole to top off the drilling mud.

vi) Grouting of the borehole will proceed until undiluted grout returns to within five feet of the surface.

vii) The borehole will be topped off with concrete to the surface.

In the event a drill rig cannot be moved into position to abandon a monitoring well or piezometer or the construction of a monitoring well prohibits abandonment using the procedure described above, the following procedure will be utilized for well abandonments:

i) The protective casing and cement pads and the breathing zone will be monitored as described in i) and ii) above.

ii) The monitoring well will be grouted using a bentonite grout mixture pumped to within five feet of the surface as described in v) above.

iii) The well casing will be cut off at grade.

iv) The remainder of the annular space will then be filled with a cement-bentonite grout mixture to the surface.

Available records indicate that MW-8 may be buried. In the event MW-8 cannot be located by visual inspection, a magnetometer will be used to identify a likely location for this well since it is constructed of iron pipe. A test excavation may then be required to positively locate this well.

H.1.4.3 HYDRAULIC DATA

H.1.4.3.1 Response Test

In situ testing will be completed to determine the hydrogeologic properties of the various stratigraphic units. Single well response tests will be performed on selected monitoring wells presented on Table H.1.4. These tests involve changing the water level within a well and monitoring the time required for the level to return to the static position. Two types of response tests are normally performed, namely: falling head tests, where a slug of known volume is introduced into the standing water column; and rising head test, where a known volume of water is removed from the well and the recovery is monitored.

The displacement of the water level will be accomplished by means of a "slug" consisting of a 1 1/2-inch diameter aluminum rod three feet in length. Alternatively, water displacement may be accomplished by removing a known volume of water from the well. The water level will be monitored with a downhole pressure transducer and a data logger until it

TABLE H.1.4

RESPONSE TEST LOCATIONS
FOUR COUNTY LANDFILL
FULTON COUNTY, INDIANA

Monitoring Well/ Piezometer ID#	*Quadrant Location*	*Screened Interval (ft amsl)* [1]	*Stratigraphic Unit*
P-29C2	NE	657.4 to 655.4	C
MW-29B	NE	729.3 to 719.3	B
MW-31B	NW	724.0 to 719.0	B
P-34*C3	NW	602.3 to 600.3	C
P-27C2	SE	671.4 to 669.4	C
P-4B	SE	720.6 to 718.6	B
P-5C4	SW	610.3 to 608.3	C
MW-24B	SW	716.9 to 711.9	B

[1] Screened interval measured in feet above mean sea level (ft amsl) datum.

Key: amsl = Above mean sea level

returns to the static level. The slug and water level measuring device will be decontaminated between wells as specified in the cleaning protocols presented in Section H.1.4.1.

Several methods have been developed for determination of hydraulic conductivity values from response test data. These methods consider well construction, hydrogeological setting, and time lag response as factors to calculate in situ hydraulic conductivity. The method of Hvorslev (1951) will be used if possible, to analyze the results of response tests. If this method is found not to be applicable, other methods which may be employed include Copper et al. (1967), Papadopoulos et al. (1973), and Bouwer and Rice (1976), and Nguyen-Pinder (1984).

H.1.4.3.2 Hydraulic Monitoring

Before purging and sampling, the water level in each monitoring well will be measured using an electronic sounding device. Water levels will be recorded in the field log book to the nearest 0.01 foot. Measuring devices will be cleaned after each use as specified in the cleaning protocols presented in Section H.1.4.1. Water levels will be measured in both new and existing monitoring wells with an electronic water level meter.

Hydraulic monitoring will be performed in accordance with the procedure outlined below:

i) Prior to conducting hydraulic monitoring at each location, electronic water level meters will be precleaned in accordance with the protocol outlined in Section H.1.3.1.

ii) The well cap will be removed and air in the breathing zone will be monitored using a photoionization detector, a combustible gas meter, a combination gas meter (O_2, CO_2, CO and H_2S) and a hydrogen cyanide gas meter in accordance with the HSP in Appendix. Samples will then don appropriate PPE consisting, at a minimum, of disposal nitrile or latex gloves.

iii) The water level meter will be self-tested and then lowered gently into the well casing. Water level meter will produce an audible and visual alarm upon encountering water within the well casing. Sampler will gently raise and lower the probe to confirm that water has been encountered.

iv) The depth to water will then be read to the nearest 0.01 foot from the top of the casing at each location. If there is a survey mark on the well casing, the depth to water will be read from that point. In the event there is no survey mark, the depth to water will be read from the north side of each well casing.

v) Depth to water level readings will be recorded in the field book. Water level tape will be removed from the well and cleaned prior to use at another location.

H.1.5.0 SAMPLING PROTOCOLS

H.1.5.1 SEDIMENT AND SURFACE WATER

Eight on-Site and 12 off-Site sediment and surface water sampling points have been identified as presented in Figures H.1.3 and H.1.4, respectively. Sediment and surface water sampling locations are approximate only. Actual sampling locations will be strategically located to be near the centerline of drainageways or swales and localized depressions or where standing water is present.

Prior to the collection of any sediment samples in the Northeast Drainage Control Basin, the Southwest Retention Pond or identified sampling locations where standing water is present, surface water samples will be collected.

Grab samples of surface water will be collected as follows:

i) A new pair of disposable latex or nitrile gloves will be donned at each location.

ii) Prior to use, sampling equipment will be decontaminated in accordance with Section H.1.4.1.

iii) Where possible, surface water samples will be collected directly into laboratory-supplied containers by gently lowering the container into the water body and allowing the container to fill. The utmost care will be utilized to minimize agitation of bottom sediments during sample collection. Samples will be collected in order of decreasing volatility.

iv) In the event grab samples cannot be collected directly into the laboratory containers, grab samples will be collected using a precleaned glass or teflon-coated dipper.

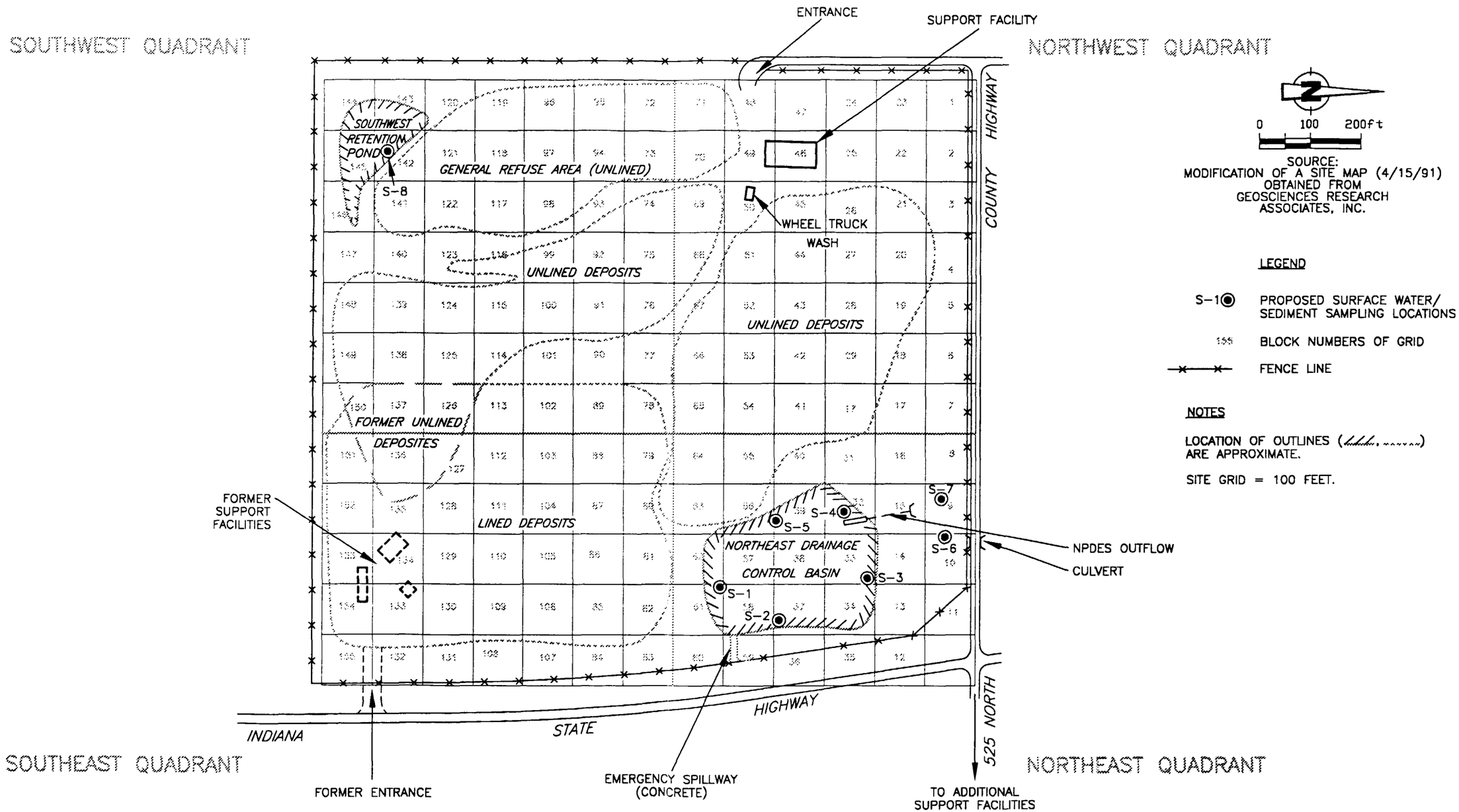

figure H.1.3

ON-SITE SURFACE WATER
AND SEDIMENT SAMPLING LOCATIONS
FOUR COUNTY LANDFILL SITE
Fulton County, Indiana

CRA

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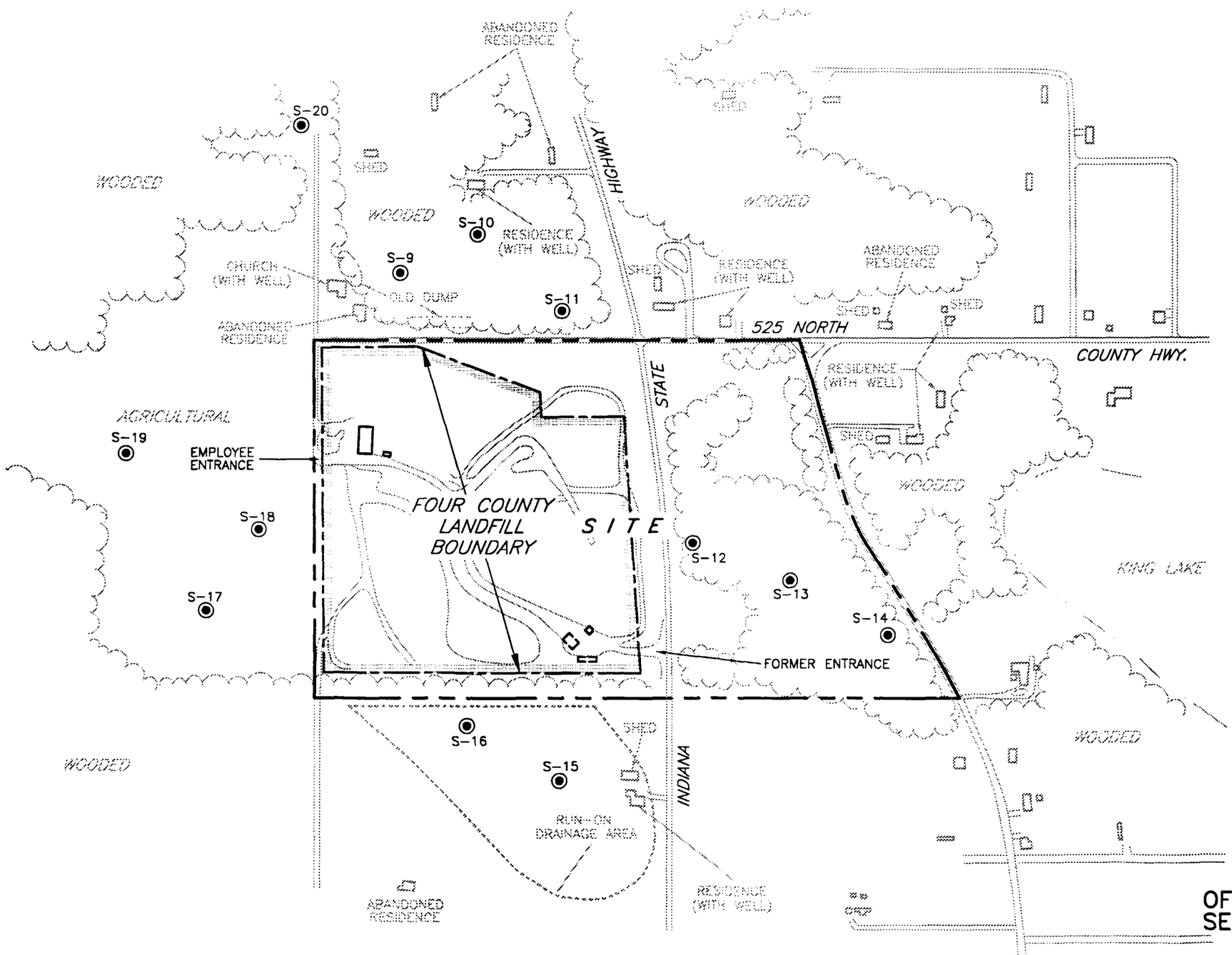

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SOURCE:
MODIFICATION OF THE
RCRA PART B PERMIT
APPLICATION (6/30/87)
PLAN SHEET NO. 1

LEGEND

S-9 PROPOSED SURFACE WATER AND SEDIMENT SAMPLING LOCATIONS

FENCE LINE

PROPERTY LINE

figure H.1.4

OFF-SITE SURFACE WATER AND SEDIMENT SAMPLING LOCATIONS
FOUR COUNTY LANDFILL
Fulton County, Indiana

CRA

5369(2) AUG. 31, 93-REV.2-(C)(P-08)

v) The sample will be labelled and then placed into a laboratory-supplied container.

vi) Collected samples will be placed immediately into a cooler containing ice pending shipment to the project laboratory. All sampling equipment will be cleaned prior to use at another sampling location.

Samples and duplicate surface water samples collected for VOC analysis will be collected directly into laboratory-supplied containers concurrently, whenever possible, to minimize volatilization. Duplicate surface water samples for other analytes will be collected in a glass or teflon lined dipper and then distributed evenly between the laboratory-supplied containers for the sample and duplicate sample. The sample and duplicate sample will be assigned unique sample identification numbers.

Sediment samples will be collected from wetland areas, drainageways and surface water bodies. Sediment sampling locations are approximate only and will be strategically located to avoid obstacles. Care will be taken to minimize the disturbance of sediments while in transit to the sampling location.

Sediment samples will be collected to a depth of 12 inches using the following protocols:

In areas where standing water is absent:

i) Samplers will don a new pair of disposable latex or nitrile gloves and appropriate PPE.

ii) Prior to use, sampling equipment will be precleaned in accordance with Section H.1.4.1.

iii) The top layer of vegetative matter, if present, will be scraped clear using a stainless-steel trowel. This procedure will be

conducted in a manner which minimizes disturbance to the topsoil or sediment beneath.

iv) A 12-inch deep excavation will be made using the stainless-steel trowel or stainless-steel bucket-type hand auger.

v) A visual inspection will be conducted of the excavation and a description of the sediment will be recorded.

vi) Sediment samples will be collected from an interval which is representative of relatively recent deposition on the basis of the visual inspection. It is assumed that the depth interval to be sampled will not exceed 6 inches.

vii) A new excavation will be made adjacent to the original excavation for the purpose of sample collection. Samples will be collected in order of decreasing analyte volatility.

viii) Samples for VOC analysis will be collected by excavating soil representative of the entire interval to be sampled. Samples collected for VOC analysis will not be homogenized but will be placed immediately into laboratory-supplied containers in a manner which minimizes headspace within the container.

ix) Samples for the remaining analytes will be collected by placing a representative aliquot of sediment into a precleaned stainless steel bowl and the sample will be homogenized. The homogenized sample will then be distributed among laboratory-supplied sample containers.

x) Collected samples will be labelled and placed into a cooler containing ice. All sampling equipment will be cleaned prior to use at another sampling location.

In areas where standing water is present:

i) The sampler will don a new pair of disposable latex or nitrile gloves. Surface water samples will be collected prior to collection of sediment samples at these locations.

ii) All sampling equipment will be precleaned as described in Section H.1.4.1.

iii) The sampler will slowly wade out to the sampling location and press a 3-inch diameter or larger stainless-steel tube or stainless-steel sediment corer into the sediments until resistance is encountered or to a maximum depth of 12 inches.

iv) The stainless-steel tube or sediment corer will be carefully removed from the sediments by gently turning or rocking the tube to loosen the sediment. The sampler will then gently remove the tube or corer from the sediment.

v) Water will be allowed to slowly drain from the tube and the sediment collected will be placed in a stainless-steel bowl.

vi) For VOC analysis, representative portion of the collected sediment will be immediately placed into a laboratory-supplied container in a manner which minimizes headspace in the container.

vii) The remaining material will be homogenized in the stainless steel bowl and distributed among the remaining containers in order of decreasing analyte volatility. If additional sample is required, steps iii) through v) will be repeated prior to homogenizing the sample until a sufficient volume of sediment has bee collected to fill the containers.

viii) Sample containers will be labelled and placed into a cooler containing ice. Sampling equipment will be cleaned prior to use at another sample location.

Duplicate sediment samples will be collected using the procedures described above except that sufficient volume will be collected for the sample and the duplicate sample. Collected sediment will be placed into a precleaned stainless-steel bowl and homogenized prior to being distributed among the laboratory-supplied containers except that duplicate samples for VOC analysis will be collected immediately and will not be homogenized prior to collection. The sample and duplicate sample will then be placed in laboratory-supplied containers in order of decreasing analyte volatility and each will be assigned a unique sample identification number.

H.1.5.2 GROUNDWATER MONITORING WELL SAMPLING PROTOCOLS

One round of groundwater samples will be collected from the 71 monitoring wells and piezometers presented on Table H.1.5. Each groundwater sample will be submitted to the laboratory and analyzed for TCL VOC, TCL SVOC, total and dissolved TAL metals, TAL total cyanide and landfill indicator parameters.

Groundwater samples will be collected in accordance with the protocols specified below:

i) The depth to water in each well will be measured to the nearest 0.01 foot using an electronic tape. The measuring device will be decontaminated prior to use following the cleaning sequence provided in Section H.1.4.1.

ii) When the well cap is removed, the concentration of vapors in the breathing zone will be monitored using a photoionization detector, a combustible gas indicator, a combination gas meter (CO_2, CO, O_2 and H_2S) and a hydrogen cyanide gas meter as described in the HSP in Appendix I. Monitoring will continue at regular intervals throughout the purging and sampling process.

iii) Prior to sampling, each well will be purged using a precleaned, stainless-steel bailer or a precleaned Grundfos Model MP-1

TABLE H.1.5

GROUNDWATER MONITORING WELL NETWORK[1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Northwest Quadrant

Monitoring Wells = 6
Piezometers = 18

MW-26	P-33A
MW-30B	P-30A
MW-31B	P-30C1
MW-32B	P-30C2
MW-33B	P-32A
MW-34*B [2]	P-32C2
P-10	P-31A
P-11A	P-31C1
P-12A	P-31C2
P-13A	P-34*A
P-14A	P-34*C1
P-26A	P-34*C2

Northeast Quadrant

Monitoring Wells = 4
Piezometers = 13

MW-20	P-23C2
MW-23B	P-28A
MW-28B	P-28C1
MW-29B	P-28C2
P-7B	
P-29A	
P-29C2	
P-8A	
P-8B	
P-8C1	
P-8C2	
P-23A	
P-23C1	

Southwest Quadrant

Monitoring Wells = 1
Piezometers = 14

MW-24B	P-5C1
P-1A	P-5C2
P-1	P-24A
P-3	P-24C1
P-6A	P-24C2
P-2A	
P-2B	
P-2C2	
P-5A	
P-5B	

Southeast Quadrant

Monitoring Wells = 5
Piezometers = 12

MW-21L	P-4A
MW-21S	P-4B
MW-21M	P-4C1
MW-25B	P-4C2
MW-27B	P-27A
P-3A	P-27C1
P-21A	P-27C2
P-25A	
P-25C2	
P-4A	

TOTALS:

Piezometers	56
Monitoring Wells	14
	71

[1] All wells known to have been installed are listed, although some may have been damaged or abandoned.
[2] A piezometer/monitoring well cluster with a numeric designation of "34*" was installed by Geosciences Research Associates between December 1988 and January 1989. The asterisk (*) is not a footnote, but rather a means of distinguishing this cluster from P-34A, also located in the northwest quadrant.

submersible stainless-steel pump equipped with precleaned reinforced PVC hose. Purging and sampling equipment will be precleaned in accordance with the protocols in Section H.1.4.1. The monitoring wells will be purged by removing a minimum of three standing well volumes of groundwater. The volume of standing water is calculated as follows:

$$V = 0.041 \ d^2 \ h$$

where:

V = volume of standing water in gallons
d = diameter of the well in inches
h = depth of water in feet

Field measurements of pH, conductivity and temperature of the purged water will be obtained and recorded in the field book following removal of each standing well volume and prior to sample collection. Field instruments will be calibrated as specified in the QAPP (Appendix H.2) prior to use. Well purging will continue until three consecutive and consistent readings (± 0.2 units for pH, ± five percent for conductivity and ± two degrees for temperature) are obtained or a maximum of five standing well volumes have been removed. Field measuring equipment will be operated in accordance with manufacturer's specifications. In the event that a well is bailed dry prior to achieving three well volumes, groundwater will be permitted to recover to a level sufficient for sample collection. The time that the well was bailed dry will be recorded and the well will be monitored for recovery. Upon recovery, the sample will be collected.

iv) After purging the required volume of well water, water samples will be collected using the decontaminated stainless-steel bailer attached to new nylon rope or Grundfos MP-1 submersible pump used during purging. If the Grundfos pump is used for sampling, the flow rate will be adjusted to a maximum of

0.1 liters/minute for collection of VOC samples. The bailer will be emptied directly into the appropriate sample containers. Containers will be filled in order of decreasing parameter volatility, using techniques which will minimize sample agitation. VOC samples will be collected in a zero headspace VOA vial. Samples collected for dissolved TAL metal analysis will be filtered through a disposable 0.45 micron filter in the field prior to preservation and analysis. Sample appearance will be recorded in the field book. The groundwater samples may be collected from the bailer used to purge the monitoring well as described above. New nylon rope will be used at each monitoring well.

v) A field duplicate sample will be collected at a frequency of one per ten investigative groundwater samples collected or at a minimum of one per sampling event. Sample containers will be filled in order of decreasing parameter volatility. Field duplicates will be assigned a unique sample identification number.

vi) Samples will be collected for matrix spike analysis at a frequency of one per each set of 20 samples collected for chemical analysis. The sample for matrix spike analysis will be collected from a well representative of the condition of the majority of the monitoring wells, turbid or non turbid. Samples will be collected from a representative monitoring well using the same protocol as for the field duplicate with increased sample volume being collected. The chain-of-custody records sent to the project laboratory will indicate the samples collected for matrix spike analysis.

vii) A field equipment rinsate blank sample will be collected at a frequency of one per ten investigative samples collected or at a minimum of one per sampling event. This sample will consist of distilled/deionized water poured into, and then sampled out of, a precleaned bailer. This will provide a quality assurance

check on the decontamination procedures employed for the bailers and sample containers. The rinsate blanks will be assigned a unique sample identification number.

viii) A trip blank will be provided by the laboratory for each sample cooler shipped containing aqueous VOC samples. Trip blanks will be analyzed for TCL VOCs to provide a check for possible sample contamination during shipping.

Purge waters generated during sampling of Site monitoring wells and piezometers will be temporarily stored in 55-gallon drums or polyethylene tanks. Purge water will be consolidated with leachate in holding tanks currently present at the Site for disposal.

H.1.6.0 ANALYTICAL PROTOCOLS

Sediment and surface water samples will be analyzed for organic analytes on the target compound list and inorganic analytes on the target analyte list. Groundwater samples will be analyzed for TCL VOC, TCL SVOC, TAL total and dissolved metals, TAL total cyanide and landfill leachate indicator parameters. Selected groundwater samples within an identified groundwater plume will be analyzed for all Appendix IX parameters, BOD and COD. A summary of the sampling and analytical program is provided on Table H.1.6.

All chemical analyses will be conducted in accordance with USEPA approved laboratory methods as discussed in the QAPP. Analytical data will be validated through a data quality assessment and validation. Data validation will be completed as discussed in the QAPP (Appendix H.2).

TABLE H.1.6

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM [1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Sample Matrix	*Field Parameters*	*Laboratory Parameters* [2]	*Investigative Samples*	*Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total*
Groundwater (first round)	pH specific conductivity temperature water level	TCL VOC, TCL SVOC, TAL total and dissolved metals, TAL cyanide, pH, sulfate, chloride, nitrate, ammonia, TDS, TSS, alkalinity	71	8	8	4	95
Groundwater (second round)	pH specific conductivity temperature water level	Full Appendix IX BOD, COD	TBD [4]	1/10 [5]	1/10	1/20 [6]	TBD
Sediment		TCL VOC, TCL SVOC TCL Pesticides/PCB, TAL Metals, TAL Cyanide	20	2	2	1	26
Surface Water	pH specific conductivity temperature water level	TCL VOC, TCL SVOC TCL Pesticides/PCB, TAL Metals, TAL Cyanide	20	2	2	1	26

1 One trip blank, which consists of two analyte-free water filled 40-mL preserved glass vials for TCL VOC water samples, will be shipped with each cooler of TCL VOC water samples.
2 TCL = Target Compound List
TAL = Target Analyte List
VOC = Volatile Organic Compounds
SVOC = Semivolatile Organic Compounds
PCB = Polychlorinated Biphenyls
TDS = Total Dissolved Solids
TSS = Total Suspended Solids
BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand
3 Matrix spike/matrix spike duplicate (MS/MSD) samples are required for organic analyses. Samples designated for MS/MSD analyses will be collected with extra volumes for aqueous samples, at a frequency of one per group of twenty (20) or fewer investigative samples. Triple the normal sample volumes will be collected for aqueous VOC samples and double the normal sample volumes will be collected for extractable organic samples. Inorganic analyses require one matrix spike/laboratory duplicate (MS/DUP) to be analyzed at a frequency of one per group of twenty (20) of fewer investigative samples.
4 To be determined based on results of the first round groundwater sampling.
5 One per 10 or fewer investigative samples.
6 One per 20 or fewer investigative samples.

APPENDIX H.2

QUALITY ASSURANCE PROJECT PLAN

QUALITY ASSURANCE PROJECT PLAN (QAPP)

LIST OF ACRONYMS AND SHORT FORMS

BOD	-	Biological Oxygen Demand
COD	-	Chemical Oxygen Demand
°C	-	Degree Centigrade
CRA	-	Conestoga-Rovers & Associates
DQO	-	Data Quality Objective
FSAP	-	Field Sampling and Analysis Plan
HLI	-	Heritage Laboratories, Inc.
IDEM	-	Indiana Department of Environmental Management
MDL	-	Method Detection Limit
MS/DUP	-	Matrix Spike/Laboratory Duplicate
MS/MSD	-	Matrix Spike/Matrix Spike Duplicate
PCB	-	Polychlorinated Biphenyls
PE	-	Performance Evaluation
PM	-	Project Manager
PRPs	-	Potentially Responsible Parties
QA	-	Quality Assurance
QA/QC	-	Quality Assurance/Quality Control
QAO	-	Quality Assurance Officer
QAPP	-	Quality Assurance Project Plan
QC	-	Quality Control
RI/FS	-	Remedial Investigation Feasibility Study
RPD	-	Relative Percent Difference
%RSD	-	Percent Relative Standard Deviation
Site	-	Four County Landfill Site; Fulton County, Indiana
SOP	-	Standard Operating Procedures
SVOC	-	Semivolatile Organic Compounds
SW-846	-	"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846
TAL	-	Target Analyte List
TCL	-	Target Compound List
TDS	-	Total Dissolved Solids
TSS	-	Total Suspended Solids
USEPA	-	United States Environmental Protection Agency
VOC	-	Volatile Organic Compounds

QUALITY ASSURANCE PROJECT PLAN (QAPP)

PROJECT TITLE: Four County Landfill Site RI/FS QAPP

PREPARED BY: CONESTOGA-ROVERS & ASSOCIATES (CRA)

Approved By: _____ Date:_____
Project Manager - CRA
Bruce Clegg

Approved by: _____ Date:_____
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Steven Wanner

Approved By: _____ Date:_____
Quality Assurance/
Quality Control Officer - Analytical Activities - CRA
Deborah Gage

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Joseph Campisi

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Heritage Laboratories, Inc.
Gary Klingler

Approved By: _____ Date:_____
QA Officer -
Heritage Laboratories, Inc.
Greg Busch

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IDEM Project Manager
Krista Duncan

QUALITY ASSURANCE PROJECT PLAN (QAPP)

PROJECT TITLE: Four County Landfill Site RI/FS QAPP

PREPARED BY: CONESTOGA-ROVERS & ASSOCIATES (CRA)

Approved By: _____ Date:_____

IDEM Quality Assurance Officer
Chemistry Section Chief
Manuela C. Johnson

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FIELD AND LABORATORY INSTRUMENTATION

H.2.1.0 INTRODUCTION

The United States Environmental Protection Agency (USEPA) and the Indiana Department of Environmental Management (IDEM) require that all environmental monitoring and measurements efforts mandated or supported by USEPA and IDEM participate in a centrally managed quality assurance (QA) program.

Any party generating data under this program has the responsibility to implement minimum procedures to assure that the precision, accuracy, completeness and representativeness of its data are known and documented. To ensure the responsibility is met uniformly, each party must prepare a written Quality Assurance Project Plan (QAPP) covering each project it is to perform.

This QAPP presents the organization, objectives, functional activities and specific quality assurance and quality control (QC) activities associated with the Remedial Investigation/Feasibility Study (RI/FS) to be conducted at the Four County Landfill Site in Fulton County, Indiana (Site). This QAPP also describes the specific protocols which will be followed for sampling, sample handling and storage, chain of custody, laboratory and field analysis.

All QA/QC procedures will be in accordance with applicable professional technical standards, USEPA and IDEM requirements, government regulations and guidelines, and specific project goals and requirements. This QAPP has been prepared by Conestoga-Rovers & Associates (CRA) in accordance with all USEPA QAPP guidance documents, in particular, Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans (QAMS-005/80) and the Region V Model QAPP (1991) and is in accordance with the QAPP requirements as specified in the Agreed Order for Remedial Investigation/Feasibility Study, Cause No. OER-92.

H.2.2.0 PROJECT DESCRIPTION

The background and history of the Site is presented in Section 2.2 of the RI/FS Work Plan.

H.2.2.1 SAMPLING NETWORK AND RATIONALE

The sampling network and rationale are presented in Section 7.0 of the RI/FS Work Plan. Specific sampling procedures are detailed in the Field Sampling and Analysis Plan (FSAP) (Section H.1 of Appendix H to the RI/FS Work Plan).

H.2.2.2 PROJECT OBJECTIVES AND SCOPE

The purpose of the RI/FS is to gather sufficient information to complete an evaluation of the nature and extent of contamination at the Site and to identify areas which pose a threat to public health, welfare or the environment.

H.2.2.3 PARAMETERS TO BE TESTED AND FREQUENCY

Sample matrices, analytical parameters and frequencies of sample collection are presented in Table H.2.1. The rationale for the selection of parameters is discussed in Section 7.0 of the RI/FS Work Plan.

H.2.2.4 DATA QUALITY OBJECTIVES (DQOs)

Data quality objectives (DQOs) are qualitative and quantitative statements which specify the quality of the data required to support decisions made during investigation activities and are based on the end uses of the data to be collected. As such, different data uses may require

TABLE H.2.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM [1]
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Sample Matrix	*Field Parameters*	*Laboratory Parameters* [2]	*Investigative Samples*	*Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total*
Groundwater (first round)	pH specific conductivity temperature water level	TCL VOC, TCL SVOC, TAL total and dissolved metals, TAL cyanide, pH, sulfate, chloride, nitrate, ammonia, TDS, TSS, alkalinity	71	8	8	4	95
Groundwater (second round)	pH specific conductivity temperature water level	Full Appendix IX BOD, COD	TBD [4]	1/10 [5]	1/10	1/20 [6]	TBD
Sediment		TCL VOC, TCL SVOC TCL Pesticides/PCB, TAL Metals, TAL Cyanide	20	2	2	1	26
Surface Water	pH specific conductivity temperature water level	TCL VOC, TCL SVOC TCL Pesticides/PCB, TAL Metals, TAL Cyanide	20	2	2	1	26

[1] One trip blank, which consists of two analyte-free water filled 40-mL preserved glass vials for TCL VOC water samples, will be shipped with each cooler of TCL VOC water samples.
[2] TCL = Target Compound List
TAL = Target Analyte List
VOC = Volatile Organic Compounds
SVOC = Semivolatile Organic Compounds
PCB = Polychlorinated Biphenyls
TDS = Total Dissolved Solids
TSS = Total Suspended Solids
BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand
[3] Matrix spike/matrix spike duplicate (MS/MSD) samples are required for organic analyses. Samples designated for MS/MSD analyses will be collected with extra volumes for aqueous samples, at a frequency of one per group of twenty (20) or fewer investigative samples. Triple the normal sample volumes will be collected for aqueous VOC samples and double the normal sample volumes will be collected for extractable organic samples. Inorganic analyses require one matrix spike/laboratory duplicate (MS/DUP) to be analyzed at a frequency of one per group of twenty (20) of fewer investigative samples.
[4] To be determined based on results of the first round groundwater sampling.
[5] One per 10 or fewer investigative samples.
[6] One per 20 or fewer investigative samples.

different levels of data quality. There are five levels of analytical support which address various data uses, the QA/QC effort and analytical methods required to achieve the desired level of quality.

DQOs have been established in accordance with the USEPA guidance document entitled "Data Quality Objectives for Remedial Response Activities - Development Process", dated March 1987, in conjunction with the document, "Data Quality Objectives for Remedial Response Activities - Example Scenario RI/FS Activities at a Facility with Contaminated Soils and Groundwater", dated March 1987. Reference to these documents ensures that the data base developed during the RI/FS activities meets the objective and quality necessary for its intended use.

DQOs can be classified for the measurement data by defining the level of analytical support assigned to each type of data measurement.

The following defines the different levels of DQO analytical support:

i) Level I - Field screening or analysis using portable instruments such as a pH meter, photoionization detector, conductivity and temperature meters and a landfill gas meter (O_2, HCN, H_2S, CO);

ii) Level II - Field analyses using more sophisticated portable analytical instruments;

iii) Level III - All analyses performed in off-Site analytical laboratories using EPA procedures other than the Contract Laboratory Program (CLP) Routine Analytical Services (RAS);

iv) Level IV - CLP-RAS performed in a CLP analytical laboratory using CLP procedures; and

v) Level V - Non-standard analytical methods performed in an off-Site laboratory.

Table H.2.2 presents the level of DQO analytical support for each group of parameters.

H.2.2.5 PROJECT SCHEDULE

The project schedule is presented in Section 13.2 of the RI/FS Work Plan.

TABLE H.2.2

LEVELS OF DATA QUALITY OBJECTIVES
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Matrix	*Analysis* [1]	*DQO*
Groundwater	TCL VOC	Level III
	TCL SVOC	Level III
	TAL Total and Dissolved Metals	Level III
	TAL Cyanide	Level III
	pH (laboratory)	Level III
	Sulfate	Level III
	Chloride	Level III
	Nitrate	Level III
	Ammonia	Level III
	TDS	Level III
	TSS	Level III
	Alkalinity	Level III
	BOD	Level III
	COD	Level III
	Full Appendix IX	Level III
	Specific Conductivity	Level I
	Water Level	Level I
	Temperature	Level I
	pH	Level I
Sediment	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCB	Level III
	TAL Metals	Level III
	TAL Cyanide	Level III
Surface Water	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCB	Level III
	TAL Metals	Level III
	TAL Cyanide	Level III
	Specific Conductivity	Level I
	Water Level	Level I
	Temperature	Level I
	pH	Level I

[1] TCL = Target Compound List
TAL = Target Analyte List
VOC = Volatile Organic Compounds
SVOC = Semivolatile Organic Compounds
PCB = Polychlorinated biphenyls
TDS = Total Dissolved Solids
TSS = Total Suspended Solids
BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand

H.2.3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Conestoga-Rovers and Associates (CRA), as consultant to the Four County Landfill PRP Group, has overall responsibility for all phases of the RI/FS at the Site. CRA will perform all sampling, well purging and field analyses.

Heritage Laboratories, Inc. (HLI) as project laboratory will perform the analyses of all samples collected during the RI/FS.

All firms will provide project management as appropriate to their responsibilities. CRA will provide administrative oversight and QA/QC for all deliverables. CRA will maintain a file copy of all laboratory deliverables. All final project deliverables will be issued by CRA.

Figure H.2.1 presents the key staff organization for the project and the associated management structure. A summary of the responsibilities of key project personnel is presented below:

Richard G. Shepherd - Principal-in-Charge - CRA
- provide overall corporate management
- participation in key technical negotiations with IDEM and Four County Landfill Technical Committee
- managerial and technical guidance to CRA's project managers

Bruce Clegg - Project Manager - CRA
- overview of field activities
- overview of laboratory activities
- managerial guidance to technical group

Steven Wanner - Project Coordinator - CRA
- data assessment
- preparation and review of reports
- evidence file custodian
- technical representation of project activities

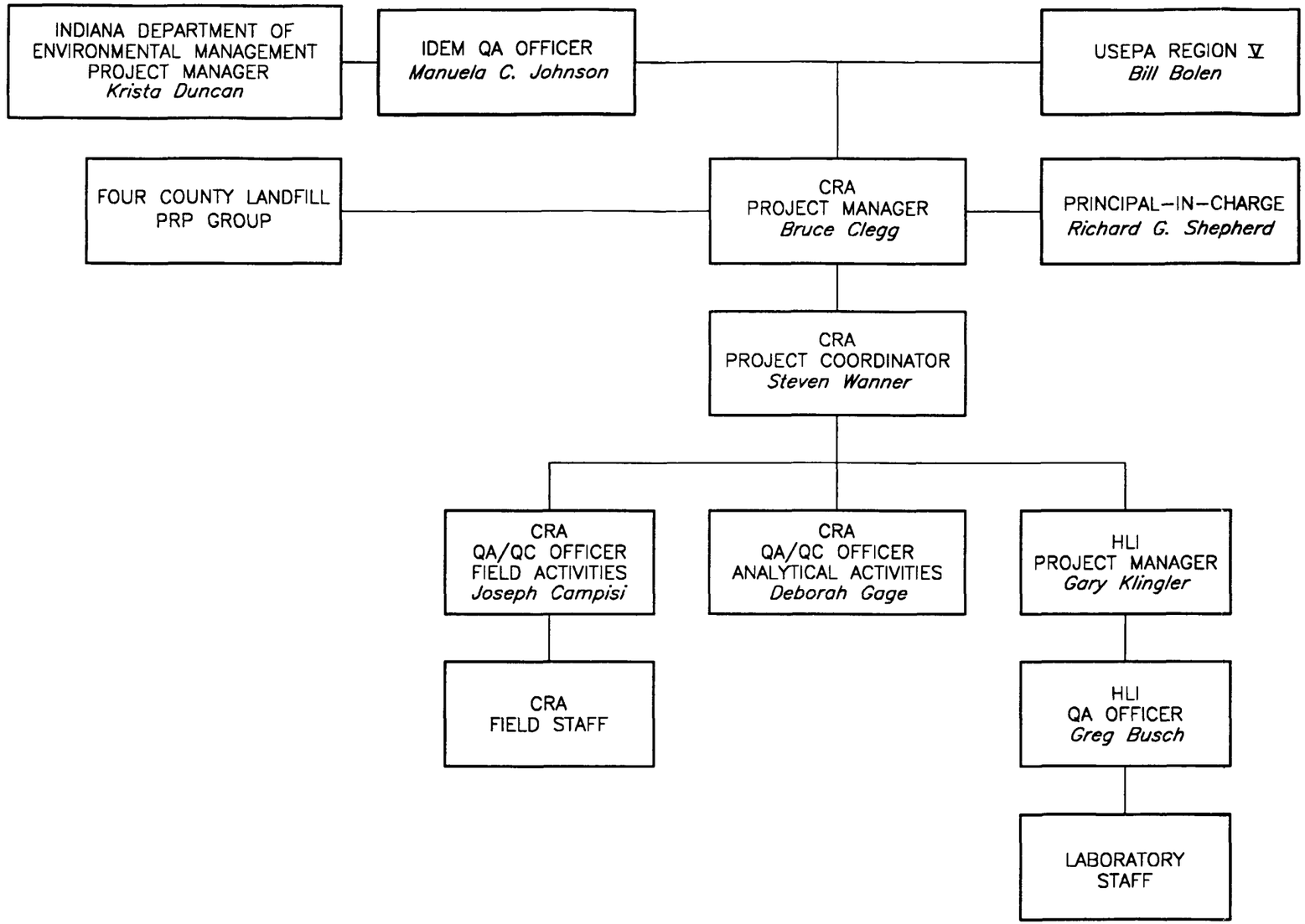

figure H.2.1
PROJECT ORGANIZATION
FOUR COUNTY LANDFILL SITE
Fulton County, Indiana

CRA

5369(2)-SEPT. 2, 93-REV.2-(C)(C-03)

Deborah Gage - QA/QC Officer - Analytical Activities - CRA

- perform laboratory system audits
- overview and review field QA/QC
- coordinate supply of performance evaluation samples
- review laboratory QA/QC
- data validation and assessment
- advise on data corrective action procedures
- preparation and review of reports
- QA/QC representation of project activities

Joseph Campisi - QA/QC Officer - Field Activities - CRA

- management of field activities and field QA/QC
- data assessment
- technical representation of field activities
- preparation of Standard Operating Procedures (SOPs) for field activities
- preparation of reports
- advise on field corrective action procedures

Gary Klingler - Project Manager - HLI

- ensures all resources of the laboratory are available on an as-required basis
- coordinate laboratory analyses
- supervise in-house chain-of-custody
- schedule sample analyses
- oversee data review
- oversee preparation of analytical reports
- overview of final analytical reports

Greg Busch - Laboratory QA Officer - HLI

- overview laboratory quality assurance
- overview QA/QC documentation
- conduct detailed data review
- decide laboratory corrective actions, if required
- technical representation of laboratory QA procedures
- preparation of laboratory SOPs
- approve final analytical reports prior to submission to CRA

Debbie Edwards - Sample Custodian - HLI

- receive and inspect the incoming sample containers
- record the condition of the incoming sample containers
- sign appropriate documents
- verify chain of custody and its correctness
- notify laboratory manager and laboratory supervisor of sample receipt and inspection
- assign a unique identification number and customer number, and enter each into the sample receiving log
- with the help of the operations manager, initiate transfer of the samples to appropriate lab sections
- control and monitor access/storage of samples and extracts

IDEM RESPONSIBILITIES

The IDEM Project Manager (PM) will be responsible for overview of this project. The PM will also be responsible for providing approval of the QAPP. Ms. Krista Duncan is the PM for the RI/FS activities. The IDEM QA Officer for the RI/FS activities is Mr. Manuela C. Johnson. The IDEM QA Officer is responsible for the final review and approval of the QAPP for IDEM.

USEPA RESPONSIBILITIES

USEPA Region V will provide technical support and review to IDEM.

H.2.4.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analyses and reporting that will provide results which are legally defensible in a court of law. Specific procedures for sampling, chain-of-custody, laboratory instruments calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field equipment and corrective action are described in subsequent sections of this QAPP. The purpose of this section is to address the specific objectives for accuracy, precision, completeness, representativeness and comparability.

H.2.4.1 LEVEL OF QA EFFORT

Field blank, trip blank, field duplicate and matrix spike samples will be analyzed to assess the quality of the data resulting from the field sampling program. Field and trip blanks consist of analyte-free water and will be submitted to the laboratory to provide the means to assess the quality of the data resulting from the field sampling program. Field blank samples are analyzed to check for procedural contamination at the Site which may cause sample contamination. Trip blanks are used to assess the potential for contamination of samples due to contaminant migration during sample shipment and storage. Field duplicate samples are analyzed to check for sampling and analytical reproducibility. Matrix spikes provide information about the effect of the sample matrix on the preparation and measurement methodology. All matrix spikes for organic analyses are performed in duplicate. Matrix spike/matrix spike duplicate (MS/MSD) samples are designated/collected for organic analyses only. A matrix spike/laboratory duplicate (MS/DUP) will be designated for inorganics analysis.

The general level of the QA effort will be one field duplicate and one field blank per ten or fewer investigative samples or a minimum of one per sampling event. One trip blank consisting of analyte-free water will be included along with each shipment of aqueous investigative VOC samples.

MS/MSD samples are designated for and collected with the investigative samples submitted for organic analyses. Aqueous MS/MSD samples must be collected at triple the volume for VOC analyses and double the normal volume for all other aqueous organic analyses. Soil MS/MSD samples do not require extra sample volume. One MS/MSD sample will be collected/designated for every 20 or fewer investigative samples per sample matrix (i.e., groundwater, sediment, surface water). MS/DUP samples are designated for the investigative samples submitted for inorganics analyses. No additional volume is required for MS/DUP analyses. One MS/DUP will be designated for every 20 or fewer investigative samples per sample matrix.

The number of field blank, field duplicate, MS/MSD and MS/DUP samples is summarized in Table H.2.1.

The level of QA effort provided by the laboratories for the samples will be consistent with the level of QA effort specified in the following documents:

i) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, 3rd edition, November 1986;

ii) "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983; and

iii) The SOPs provided in Attachment H.2-1 to Appendix H.2 (Attachment H.2-1).

The QA level of effort for the field measurements of pH and specific conductance will be as described in the SOPs in Attachment H.2-1. Temperature readings will be obtained with the pH measurements. Water level will be measured to the nearest 0.01 ft. using an electric sounding water level meter.

H.2.4.2 ACCURACY, PRECISION AND SENSITIVITY OF ANALYSES

The fundamental QA objective with respect to accuracy, precision, and sensitivity of laboratory analytical data is to achieve the QC acceptance criteria of the analytical protocols.

SOPs for the laboratory analyses are provided in Attachment H.2-1. SOPs for the field equipment to measure pH, conductivity and temperature are provided in Attachment H.2-1. These include the accuracy and precision required for the analyses. The sensitivity required for the analyses is presented in Tables H.2.3 through H.2.8 of this QAPP.

H.2.4.3 COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is expected that HLI will provide data meeting the QC acceptance criteria for 80 percent or more of all samples tested using the specified methods. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness} = \frac{\text{Valid (usable) Data Obtained}}{\text{Total Data Planned}} \times 100$$

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition or an environmental condition. Representativeness is a qualitative parameter which is dependent upon the proper design of the sampling program and proper laboratory protocol. The sampling network was designed to provide data representative of Site conditions. During development of this network, consideration was given to the historical plant operations, existing analytical data and physical setting and processes. The rationale of the sampling network is discussed in

TABLE H.2.3

TARGETED QUANTITATION LIMITS FOR TCL VOLATILE ORGANIC COMPOUNDS ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

		Targeted Quantitation Limits [1]	
Cas No.	*Compound*	*Water (µg/L)*	*Sediment* [2] *(µg/kg)*
TCL Volatile Organic Compounds			
67-64-1	acetone	10	50
71-43-2	benzene	1	5
75-27-4	bromodichloromethane	1	5
75-25-2	bromoform	1	5
74-83-9	bromomethane	1	10
78-93-3	butanone	10	50
75-15-0	carbon disulfide	1	5
56-23-5	carbon tetrachloride	1	5
108-90-7	chlorobenzene	1	5
75-00-3	chloroethane	1	10
67-66-3	chloroform	1	5
74-87-3	chloromethane	1	10
10061-01-15	cis-1,3-dichloropropene	1	5
124-48-1	dibromochloromethane	1	5
75-35-3	1,1-dichloroethane	1	5
107-06-2	1,2-dichloroethane	1	5
75-35-4	1,1-dichloroethene	1	5
540-59-0	1,2-dichloroethene (total)	1	5
78-87-5	1,2-dichloropropane	1	5
100-41-4	ethylbenzene	1	5
591-78-6	2-hexanone	10	50
75-09-2	methylene chloride	1	5
108-10-1	4-methyl-2-pentanone	10	50
100-42-5	styrene	1	5
79-34-5	1,1,2,2-tetrachloroethane	1	5
127-18-4	tetrachloroethene	1	5
108-88-3	toluene	1	5
10061-02-6	trans-1,3-dichloropropene	1	5
71-55-6	1,1,1-trichloroethane	1	5
79-00-5	1,1,2-trichloroethane	1	5
79-01-6	trichloroethene	1	5
75-01-4	vinyl chloride	1	10
1330-20-7	xylenes (total)	1	5

[1] Actual sample quantitation limits are highly matrix dependent. Targeted quantitation limits presented are for guidance only.

[2] The targeted quantitation limits for sediment are based on wet weight. The data will be reported on a dry weight basis; therefore, the quantitation limits will be higher depending upon the percent moisture of each sample.

TABLE H.2.4

TARGETED QUANTITATION LIMITS FOR TCL
SEMIVOLATILE ORGANIC COMPOUNDS ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

		Targeted Quantitation Limits [1]	
CAS No.	*Compound*	*Water (µg/L)*	*Sediment* [2] *(µg/kg)*
TCL Semivolatile Organic Compounds			
83-32-9	acenaphthene	10	330
208-96-8	acenaphthylene	10	330
120-12-7	anthracene	10	330
56-55-3	benzo(a)anthracene	10	330
50-32-8	benzo(a)pyrene	10	330
205-99-2	benzo(b)fluoranthene	10	330
191-24-2	benzo(g,h,i)perylene	10	330
207-08-9	benzo(k)fluoranthene	10	330
111-91-1	bis(2-chloroethoxy)methane	10	330
111-44-4	bis(2-chloroethyl)ether	10	330
108-60-1	bis(2-chloroisopropyl)ether	10	330
117-81-7	bis(2-ethylhexyl)phthalate	10	330
85-68-7	butylbenzylphthalate	10	330
101-55-3	4-bromophenylphenyl ether	10	330
86-74-8	carbazole	10	330
106-47-8	4-chloroaniline	10	330
91-58-7	2-chloronaphthalene	10	330
7005-72-3	4-chlorophenyl phenyl ether	10	330
218-01-9	chrysene	10	330
53-70-3	dibenz(a,h)anthracene	10	330
132-64-9	dibenzofuran	10	330
95-50-1	1,2-dichlorobenzene	10	330
541-73-1	1,3-dichlorobenzene	10	330
106-46-7	1,4-dichlorobenzene	10	330
91-94-1	3,3'-dichlorobenzidine	50	660
84-66-2	diethylphthalate	10	330
131-11-3	dimethylphthalate	10	330
84-74-2	di-n-butyphthalate	10	330
117-84-0	di-n-octylphthalate	10	330
121-14-2	2,4-dinitrotoluene	10	330
606-20-2	2,6-dinitrotoluene	10	330
206-44-0	fluoranthene	10	330
86-73-7	fluorene	10	330
118-74-1	hexachlorobenzene	10	330
87-68-3	hexachlorobutadiene	10	330

TABLE H.2.4

TARGETED QUANTITATION LIMITS FOR TCL
SEMIVOLATILE ORGANIC COMPOUNDS ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

		Targeted Quantitation Limits [1]	
CAS No.	*Compound*	*Water* (µg/L)	*Sediment* [2] (µg/kg)
77-47-4	hexachlorocyclopentadiene	10	330
67-72-1	hexachloroethane	10	330
193-39-5	indeno(1,2,3-cd)pyrene	10	330
78-59-1	isophorone	10	330
91-57-6	2-methylnaphthalene	10	330
91-20-3	naphthalene	10	330
88-74-4	2-nitroaniline	50	1,600
99-09-2	3-nitroaniline	50	1,600
100-01-6	4-nitroaniline	50	1,600
98-95-3	nitrobenzene	10	330
621-64-7	N-nitroso-di-n-propylamine	10	330
86-30-6	N-nitrosodiphenylamine (diphenylamine)	10	330
85-01-8	phenanthrene	10	330
129-00-0	pyrene	10	330
120-82-1	1,2,4-trichlorobenzene	10	330
59-50-7	4-chloro-3-methylphenol	10	330
95-57-8	2-chlorophenol	10	330
120-83-2	2,4-dichorophenol	10	330
105-67-9	2,4-dimethylphenol	10	330
51-28-5	2,4-dinitrophenol	50	1,600
534-52-1	4,6-dinitro-2-methylphenol	50	1,600
95-48-7	2-methylphenol	10	330
106-44-5	4-methylphenol	10	330
88-75-5	2-nitrophenol	10	330
100-02-7	4-nitrophenol	50	1,600
87-86-5	pentachlorophenol	50	1,600
108-95-2	phenol	10	330
95-95-4	2,4,5-trichlorophenol	50	1,600
88-06-2	2,4,6-trichlorophenol	10	330

[1] Actual sample quantitation limits are highly matrix dependent. Targeted quantitation limits presented are for guidance only.

[2] The targeted quantitation limits for sediment are based on wet weight. The data will be reported on a dry weight basis; therefore, the quantitation limits will be higher depending upon the percent moisture of each sample.

TABLE H.2.5

TARGETED QUANTITATION LIMITS FOR TCL PESTICIDES/PCB
ORGANIC COMPOUNDS ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

		Targeted Quantitation Limits [1]	
Cas No.	*Compound*	*Water* (µg/L)	*Sediment* [2] (µg/kg)
TCL Pesticides/PCB			
319-84-6	alpha-BHC	0.05	1.7
319-85-7	beta-BHC	0.05	1.7
319-86-8	delta-BHC	0.05	1.7
58-89-9	gamma-BHC	0.05	1.7
76-44-8	heptachlor	0.05	1.7
309-00-2	aldrin	0.05	1.7
1024-57-3	heptachlor expoxide	0.05	1.7
959-98-8	endosulfan I	0.05	1.7
60-57-1	dieldrin	0.1	3.3
72-55-9	4,4'-DDE	0.1	3.3
72-20-8	endrin	0.1	3.3
33213-65-9	endosulfan II	0.1	3.3
72-54-8	4,4'-DDD	0.1	3.3
1031-07-8	endosulfan sulfate	0.1	3.3
50-29-3	4,4'-DDT	0.1	3.3
72-43-5	methoxychlor	0.5	17.0
53494-70-5	endrin ketone	0.1	3.3
7421-36-3	endrin aldehyde	0.1	3.3
5103-71-9	alpha-chlordane	0.5	1.7
5103-74-2	gamma-chlordane	0.5	1.7
8001-35-2	toxaphene	5.0	170.0
12674-11-2	PCB-1016	1.0	33.0
11104-28-2	PCB-1221	2.0	67.0
11141-16-5	PCB-1232	1.0	33.0
53469-21-9	PCB-1242	1.0	33.0
12672-29-6	PCB-1248	1.0	33.0
11097-69-1	PCB-1254	1.0	33.0
11096-82-5	PCB-1260	1.0	33.0

1 Actual sample quantitation limits are highly matrix dependent. Targeted quantitation limits presented are for guidance only.

2 The targeted quantitation limits for sediment are based on wet weight. The data will be reported on a dry weight basis; therefore, the quantitation limits will be higher depending upon the percent moisture of each sample.

TABLE H.2.6

TARGETED QUANTITATION LIMITS FOR TAL INORGANICS ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limits [1]	
	Water (µg/L)	*Sediment* [2] *(mg/kg)*
TAL Inorganics		
aluminum	200	40
antimony	60	12
arsenic	10	2
barium	200	40
beryllium	5	1
cadmium	5	1
calcium	5,000	1,000
chromium	10	2
cobalt	50	10
copper	25	5
iron	100	20
lead	3	0.6
magnesium	5,000	1,000
manganese	15	3
mercury	0.2	0.10
nickel	40	8
potassium	5,000	1,000
selenium	5	1
silver	10	2
sodium	5,000	1,000
thallium	10	2
vanadium	50	10
zinc	20	4
cyanide	10	2

[1] Actual sample quantitation limits are highly matrix dependent. Targeted quantitation limits presented are for guidance only.

[2] The targeted quantitation limits for sediment are based on wet weight. The data will be reported on a dry weight basis; therefore, the quantitation limits will be higher depending upon the percent moisture of each sample.

TABLE H.2.7

TARGETED QUANTITATION LIMITS FOR
GENERAL CHEMISTRY ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limits [1]
	Water (mg/L)
General Chemistry Parameter	
sulfate	5
chloride	5
nitrate	0.01
ammonia	0.10
TDS	10
TSS	1.0
alkalinity	1.0
BOD	1.0
COD	10

[1] Actual sample quantitation limits are highly matrix dependent. Targeted quantitation limits presented are for guidance only.

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water (µg/L)
Volatiles	
Acetone	50
Acetonitrile	50
Acrolein	100
Acrylonitrile	70
Allyl chloride (3-chloropropene)	20
Benzene	5
Bromodichloromethane	5
Bromoform	10
Bromomethane	10
2-Butanone (MEK)	50
Carbon disulfide	5
Carbon tetrachloride	10
Chlorobenzene	5
Chloroethane	10
Chloroform	5
Chloromethane	10
Chloropropene (2-chlorobutadiene-1,3)	20
Dibromochloromethane	5
1,2-Dibromo-3-chloropropane (DBCP)	20
1,2-Dibromoethane (EDB)	20
Dibromomethane	5
trans-1,4-Dichloro-2-butene	20
Dichlorodifluoromethane	20
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
1,2-Dichloroethene (total)	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
1,4-Dioxane	1,000
Ethylbenzene	5
Ethyl methacrylate	20
Iodomethane	20
Isobutanol	1,000
2-Hexanone	50
Methacrylonitrile	20
Methylene chloride	5
Methyl methacrylate	20
4-Methyl-2-pentanone (MIBK)	50

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water (µg/L)
Volatiles Continued	
Propionitrile (Ethyl cyanide)	100
Styrene	5
1,1,1,2-Tetrachloroethane	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
1,2,3-Trichloropropane	5
Vinyl acetate	50
Vinyl chloride	10
Xylenes (total)	5
Semivolatiles	
Acenaphthene	10
Acenaphthylene	10
Acetophenone	10
2-Acetylaminofluorene	20
4-Aminobiphenyl	50
Aniline	10
Anthracene	10
Aramite	50
Benzo(a)anthracene	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(g,h,i)perylene	10
Benzo(a)pyrene	10
Benzyl alcohol	10
4-Bromophenyl phenyl ether	10
Butyl benzyl phthalate	10
4-Chloroaniline	10
Chlorobenzilate	10
bis(2-Chloroethoxy)methane	10
bis(2-Chloroethyl)ether	10
bis(2-Chloroisopropyl)ether	10
4-Chloro-3-methylphenol	10
2-Chloronaphthalene	10

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water (µg/L)
Semivolatiles Continued	
2-Chlorophenol	10
4-Chlorophenyl phenyl ether	10
Chrysene	10
Diallate	10
Dibenz(a,h)anthracene	10
Dibenzofuran	10
Di-n-butyl phthalate	10
1,2-Dichlorobenzene	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
3,3'-Dichlorobenzidine	20
2,4-Dichlorophenol	10
2,6-Dichlorophenol	10
Diethyl phthalate	10
Dimethoate	10
p-Dimethylaminoazobenzene	10
7,12-Dimethylbenz(a)anthracene	20
3,3'-Dimethylbenzidine	20
a,a-Dimethylphenethylamine	10
2,4-Dimethylphenol	10
Dimethyl phthalate	10
1,3-Dinitrobenzene	10
4,6-Dinitro-2-methylphenol	50
2,4-Dinitrophenol	50
2,4-Dinitrotoluene	10
2,6-Dinitrotoluene	10
Dinoseb	10
Di-n-octyl phthalate	10
Diphenylamine	10
Disulfoton	10
bis(2-Ethylhexy)phthalate	10
Ethyl methanesulfonate	10
Ethyl parathion	10
Famphur	10
Fluoranthene	10
Fluorene	10
Hexachlorobenzene	10
Hexachlorobutadiene	10
Hexachlorocyclopentadiene	10
Hexachloroethane	10
Hexachlorophene	50

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water (*µg/L*)
Semivolatiles Continued	
Hexachloropropene	200
Indeno (1,2,3-cd)pyrene	10
Isodrin	20
Isophorone	10
Isosafrole	10
Kepone	20
Methapyrilene	100
3-Methylcholanthrene	100
Methyl methanesulfonate	10
2-Methylnaphthalene	10
Methyl parathion	10
2-Methylphenol	10
4-Methylphenol	10
Naphthalene	10
1,4-Naphthoquinone	200
1-Naphthylamine	50
2-Naphthylamine	10
2-Nitroaniline	50
3-Nitroaniline	50
4-Nitroaniline	50
Nitrobenzene	10
2-Nitrophenol	10
4-Nitrophenol	50
4-Nitroquinoline-1-oxide	100
N-Nitroso-di-n-butylamine	10
N-Nitrosodiethylamine	10
N-Nitrosodimethylamine	10
N-Nitrosodiphenylamine	10
N-Nitroso-di-n-propylamine	10
N-Nitrosomethylethylamine	10
N-Nitrosomorpholine	10
N-Nitrosopiperidine	10
N-Nitrosopyrrolidine	10
5-Nitro-o-toluidine	10
Pentachlorobenzene	10
Pentachloroethane	50
Pentachloronitrobenzene	50
Pentachlorophenol	50
Phenacetin	50
Phenanthrene	10
Phenol	10

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water (*µg/L*)
Semivolatiles Continued	
4-Phenylenediamine	50
Phorate (Thimet)	10
2-Picoline	50
Pronamide	20
Pyrene	10
Pyridine	50
Safrole	10
Sulfotepp	10
1,2,4,5-Tetrachlorobenzene	10
2,3,4,6-Tetrachlorophenol	50
Thionazin	10
2-Toluidine	10
1,2,4-Trichlorobenzene	10
2,4,5-Trichlorophenol	10
2,4,6-Trichlorophenol	10
0,0,0-Triethyl phosphorothioate	10
1,3,5-Trinitrobenzene	50
Pesticides/PCBs	
Aldrin	0.05
Aroclor 1016	0.5
Aroclor 1221	0.5
Aroclor 1232	0.5
Aroclor 1242	0.5
Aroclor 1248	0.5
Aroclor 1254	1
Aroclor 1260	1
alpha-BHC	0.05
beta-BHC	0.05
delta-BHC	0.05
gamma-BHC (Lindane)	0.05
Chlordane	0.5
4,4'-DDD	0.1
4,4'-DDE	0.1
4,4'-DDT	0.1
Dieldrin	0.1
Endosulfan I	0.05
Endosulfan II	0.1
Endosulfan sulfate	0.1

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water
	(µg/L)
Pesticides/PCBs continued	
Endrin	0.1
Endrin aldehyde	0.1
Heptachlor	0.05
Heptachlor epoxide	0.05
Methoxychlor	0.5
Toxaphene	1
Chlorinated Herbicides	
2,4-D	10
2,4,5-T	1.0
2,4,5-TP (Silvex)	1.0
Inorganics	
Antimony	300
Barium	10
Beryllium	5
Cadmium	10
Chromium	20
Cobalt	50
Copper	10
Nickel	40
Silver	10
Tin	1,000
Vanadium	50
Zinc	50
Arsenic	5
Lead	3
Mercury	0.2
Thallium	10
Cyanide	10
Sulfide	1,000
Selenium	5

TABLE H.2.8

TARGETED QUANTITATION LIMITS FOR APPENDIX IX LIST PARAMETER LIST
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Targeted Quantitation Limit [1]
	Water (µg/L)
TCDD [2]	
2,3,7,8-TCDD	100

[1] Actual sample quantitation limits are highly matrix dependent. Targeted quantitation limits presented are for guidance only. Targeted quantitation limits may be affected by moisture content, matrix interferences, QA/QC problems and high concentrations of target and non-target analytes.

[2] Sample specific quantitation limits will be calculated for 2,3,7,8-TCDD based upon the signal to noise ratio.

detail in the RI/FS Work Plan. Representativeness will be satisfied by insuring that the RI/FS Work Plan is followed, proper sampling techniques are used, proper analytical procedures are followed and holding times of the samples are not exceeded in the laboratory.

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of sampling and analytical methods. The procedures used to obtain the planned analytical data, as documented in the QAPP, are expected to provide comparable data. However, these new analytical data may not be directly comparable to existing data because of differences in procedures and QA objectives.

H.2.4.4 FIELD MEASUREMENTS

Measurement data will be generated in many field activities. These activities include, but are not limited to, the following:

i) documenting time and weather conditions;

ii) determining pH, specific conductivity, and temperature of groundwater and surface water samples;

iii) verifying well development and pre-sampling purge volumes; and

iv) determining well water levels.

The general QA objective for such measurement data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the use of standardized procedures.

H.2.5.0 SAMPLING PROCEDURES

Procedures and protocols for collecting samples and for performing all related field activities are presented in the FSAP (Appendix H.1).

H.2.6.0 SAMPLE CUSTODY AND DOCUMENT CONTROL

It is IDEM and Region V Policy to follow the USEPA Region V sample custody, or the chain-of-custody protocols as described in "NEIC Policies and Procedures", EPA-330/9-78-001-R, revised August 1991. This custody is in three parts: sample collection, laboratory analysis and final evidence files. Final evidence files, including all originals of laboratory reports are maintained under document control in a secure area.

A sample or evidence file is in your custody if it:

i) is in your possession;

ii) is in your view, after being in your possession;

iii) is in your possession and you place them in a secured location; or

iv) is in a designated secure area.

H.2.6.1 FIELD CHAIN-OF-CUSTODY PROCEDURES

The sample packaging and shipment procedures summarized below will insure that the samples will arrive at the laboratory with the chain-of-custody intact. The protocol for specific sample numbering using case numbers and traffic report numbers, if applicable, and other sample designations are included in the FSAP.

H.2.6.1.1 Field Procedures

1) The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched to the laboratory. As few people as possible should handle the samples.

2) All bottles will be labeled with unique sample numbers.

3) Sample labels are to be completed for each sample using waterproof ink.

H.2.6.1.2 Field Logbooks/Documentation

Field logbooks will be used to record the data collecting activities performed. As such, entries will be described in as much detail as possible so that persons going to the Site could reconstruct a particular situation without reliance on memory.

The title page of each logbook will contain the following:

i) person to whom the logbook is assigned;

ii) logbook number;

iii) project name;

iv) project start date; and

v) end date.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the Site and the purpose of their visit will also be recorded in the field logbook.

Measurements made and samples collected will be recorded in the field logbook. All entries will be made in ink with no erasures. If an incorrect entry is made, the information will be crossed out

with a single strike mark. Whenever a sample is collected, or a measurement is made, a detailed description of the location of the sampling point which includes compass direction and distance taken from a reference point will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Copies of all field book entries will be provided to IDEM as part of the monthly report.

Samples will be collected following the sampling procedures documented in the FSAP. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth from which the sample was collected, volume of sample and number of containers. A unique sample identification number will be assigned during sample collection. Field QC samples, which will receive unique sample identification numbers, will be submitted to the laboratory blind to avoid laboratory bias of field QC samples.

Table H.2.9 presents the container, preservation, shipping and packaging requirements for the samples to be collected. Container cleaning procedures will be consistent with "Specification and Guidance for Obtaining Contaminant-Free Sample Containers", OSWER Directive #9240.0-05A, April 1992. The laboratory will use Eagle-Pitcher or equivalent sample containers.

H.2.6.1.3 Transfer of Custody and Shipment Procedures

1. Samples are accompanied by a properly completed chain-of-custody record. The sample numbers and locations will be listed on the chain-of-custody record. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to the laboratory, or to/from a secure storage area.

TABLE H.2.9

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Analyses	*Sample Containers*	*Preservation*	*Maximum Holding Time from Sample Collection**	*Volume of Sample*	*Shipping*	*Normal Packaging*
Groundwater						
TCDD	Two 1-liter amber glass bottles	Iced, 4 °C	30 days for extraction 45 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL SVOC, Appendix IX SVOC, Appendix IX Pest/PCB, Appendix IX Herbicides	Two 1-liter amber glass bottles per analysis	Iced, 4° C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL VOC, Appendix IX VOC	Three 40-mL teflon lined septum vials per analysis	HCl to pH <2, Iced, 4 °C	14 days for analysis	Fill completely, no air bubbles	Federal Express Priority 1	Foam Liner
TAL Total Metals, TAL Dissolved Metals, Appendix IX Metals	One 1-liter plastic bottle per analysis	HNO3 to pH <2, Iced, 4 °C	6 months (mercury - 28 days) for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Cyanide	One 1-liter plastic bottle	NaOH to pH >12, Iced, 4 °C	14 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
BOD	One 1-liter polyethylene	Iced, 4 °C	48 hours to incubation	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Total Suspended Solids, Total Dissolved Solids	One 1-liter polyethylene	Iced, 4 °C	7 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Alkalinity, Chloride, Sulfate	One 1-liter polyethylene	Iced, 4 °C	28 days (Alkalinity 14 days) for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips

TABLE H.2.9

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Analyses	*Sample Containers*	*Preservation*	*Maximum Holding Time from Sample Collection**	*Volume of Sample*	*Shipping*	*Normal Packaging*
Ammonia, Nitrate, COD	One 1-liter polyethylene	H2SO4 to pH<2 Iced, 4 °C	28 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Sediment						
TCL SVOC, TCL Pesticides/PCB	One 8-ounce glass per analysis	Iced, 4 °C	14 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL VOC	One 4-ounce glass	Iced, 4 °C	14 days for analysis	Fill completely	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Metals	One 16-ounce glass	Iced, 4 °C	6 months (mercury - 28 days) for analysis	Fill to shoulder of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Cyanide	No additional jar necessary	Iced, 4 °C	14 days for analysis	Fill to shoulder of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
Surface Water						
TCL SVOC, TCL Pesticides/PCB	Two 1-liter amber glass bottles per analysis	Iced, 4 °C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TCL VOC	Three 40-mL teflon lined septum vials	HCl to pH <2, Iced, 4 °C	14 days for analysis	Fill completely, no air bubbles	Federal Express Priority 1	Foam Liner
TAL Metals	One 1-liter plastic bottle	HNO3 to pH <2, Iced, 4 °C	6 months (mercury - 28 days) for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap or Foam Chips
TAL Cyanide	One 1-liter plastic bottle	NaOH to pH >12, Iced, 4 °C	14 days for analysis	Fill to neck of bottle	Federal Express	Bubble Wrap or Foam Chips

* - These are technical holding times; (i.e., are based on time elapsed from time of sample collection).

2. Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be secured with strapping tape and custody seals for shipment to the laboratory. This procedure includes use of a custody seal attached to the front right and back left of the cooler. The custody seals are covered with clear plastic tape. The cooler is strapped shut with strapping tape in at least two locations.

3. Whenever samples are split with another party, a separate chain-of-custody record is prepared for those samples and marked to indicate with whom the samples are being split. The person relinquishing the samples to the other party should request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses to sign, this is noted in the "Received By" space.

4. All shipments will be accompanied by the chain-of-custody record identifying the contents. The original record and yellow copy will accompany the shipment, and the pink and goldenrod copies will be retained by shipper (if different than the sampler) and the sampler for their files.

5. If the samples are sent by commercial carrier, a bill of lading will be used. Receipts of bills of lading will be retained as part of the permanent custody documentation. Commercial carriers are not required to sign off on the custody record provided the custody forms are sealed inside the sample cooler and the custody seals remain intact.

H.2.6.2 LABORATORY CHAIN-OF-CUSTODY PROCEDURES

The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number and

customer number will then be entered into the sample receiving log. The laboratory date of receipt will also be noted.

Laboratory custody procedures and document control for those samples analyzed by the project laboratory will be carried out as specified in the appropriate SOP included in Attachment H.2-1.

H.2.6.3 STORAGE OF SAMPLES

After the sample custodian has prepared the logbook, the chain-of-custody results will be checked to ensure that all samples are stored in the appropriate locations. All samples will be stored within an access controlled location and will be maintained preserved (as specified in Table H.2.9) until completion of all analytical work or, at a minimum, for 30 days after receipt of the final report by CRA.

H.2.6.4 FINAL EVIDENCE FILES CUSTODY PROCEDURES

Evidential files for the entire project will be maintained by CRA and will consist of the following:

i) project plan;

ii) project logbooks;

iii) field data records;

iv) sample identification documents;

v) chain-of-custody records;

vi) correspondence;

vii) references, literature;

viii) final data packages;

ix) miscellaneous - photos, maps, drawings, etc.; and

x) final report.

The evidentiary file materials will be the responsibility of the evidentiary file custodian with respect to maintenance and document removal.

The laboratory will be responsible for maintaining analytical logbooks and laboratory data. Raw laboratory data files will be inventoried and maintained by the laboratory for a period of six years, at which time CRA will advise the laboratory regarding the need for additional storage.

H.2.7.0 CALIBRATION PROCEDURES AND FREQUENCY

This section describes or references the procedures for maintaining the accuracy for the instruments and measuring equipment which will be used for performing field measurements and laboratory analyses. These instruments and equipment will be calibrated or the calibration verified prior to each use or according to a periodic schedule.

H.2.7.1 FIELD INSTRUMENTS/EQUIPMENT

Instruments and equipment used to gather, generate or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specification.

Equipment to be used during the field sampling will be examined to certify that it is in operating condition. This includes checking the manufacturer's operating manual for each instrument to ensure that all maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that notations on any prior equipment problem are not overlooked, and all necessary repairs to equipment have been carried out.

H.2.7.1.1 Field Instrument Calibration

Calibration of the field instruments will be performed prior to the collection of each water sample if well purging data indicate a change (>±10 percent) in pH and/or conductivity from the last location sampled. Calibration of field instruments will be performed daily during groundwater sampling and the calibration will be checked after a maximum of 10 samples and the end of sample analysis. The field equipment will be maintained, calibrated and operated in a manner consistent with the manufacturer's guidelines and the SOPs in Attachment H.2-1.

Water levels will be measured to the nearest 0.01 foot using an electronic sounding water level meter. No field calibration is possible.

H.2.7.2 LABORATORY INSTRUMENTS

Calibration of laboratory equipment will be based on approved written procedures. Records of calibration, repairs, or replacement of instruments will be filed and maintained by the designated laboratory personnel performing quality control activities. These records will be filed at the location where the work is performed and will be subject to QA audit. For all instruments, the laboratory will maintain a factory-trained repair staff with in-house spare parts or will maintain service contracts with vendors.

The records of calibration will be kept as follows:

1) If possible, each instrument will have record of calibration permanently affixed with an assigned record number.

2) A label will be affixed to each instrument showing description, manufacturer, model numbers, date of last calibration and by whom calibrated (signature), due date of next calibration and compensation or correction figures, as appropriate.

3) A written calibration procedure will be available for each piece of test and measurement equipment.

4) Any instrument that is not calibrated within the manufacturer's original specification will display an appropriate warning tag.

Specific calibration procedures are detailed in the respective methods and the associated SOPs as presented in Attachment H.2-1.

H.2.8.0 ANALYTICAL PROCEDURES

The sediment, surface water and groundwater samples collected for chemical analyses will be analyzed using the methods presented in Table H.2.10.

TABLE H.2.10

SUMMARY OF ANALYTICAL METHODS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

	Parameter[1]	*Analytical Methods*		*Preparatory Methods*[2]
Groundwater	TCL VOC	SW-846[3]	8260A	
	TCL SVOC	SW-846	8270A	SW-846 3510A/3520A
	TAL Total and Dissolved Metals	SW-846	6010A/7000A series	SW-846 3010A/3020A
	TAL Cyanide	SW-846	9012	
	pH	USEPA[4]	150.1	
	Sulfate	USEPA	375.4	
	Chloride	USEPA	325.2	
	Nitrate	USEPA	352.1	
	Ammonia	USEPA	350.2	
	TDS	USEPA	160.1	
	TSS	USEPA	160.2	
	Alkalinity	USEPA	370.1	
	BOD	USEPA	405.1	
	COD	USEPA	410.1	
	Appendix IX VOC	SW-846	8240A	
	Appendix IX SVOC	SW-846	8270A	SW-846 3510A/3520A
	Appendix IX Pesticides/PCB	SW-846	8080A	SW-846 3510A/3520A
	Appendix IX Metals	SW-846	6010A/7000A series	SW-846 3010A/3520A
	Appendix IX Herbicides	SW-846	8150A	
	Appendix IX TCDD	SW-846	8290	
Sediment	TCL VOC	SW-846	8240A	
	TCL SVOC	SW-846	8270A	SW-846 3550A
	TCL Pesticides/PCB	SW-846	8080	SW-846 3550A
	TAL Metals	SW-846	6010/7000 series	SW-846 3050A
	TAL Cyanide	SW-846	9012	
Surface Water	TCL VOC	SW-846	8260A	
	TCL SVOC	SW-846	8270A	SW-846 3510A/3520A
	TCL Pesticides/PCB	SW-846	8080	SW-846 3510A/3520A
	TAL Metals	SW-846	6010A/7000A series	SW-846 3010A/3020A
	TAL Cyanide	SW-846	9012	

[1] TCL = Target Compound List
TAL = Target Analyte List
VOC = Volatile Organic Compounds
SVOC = Semivolatile Organic Compounds
PCB = Polychlorinated Biphenyls
TDS = Total Dissolved Solids
TSS = Total Suspended Solids
BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand
TCDD = 2,3,7,8-Tetrachlorodibenzo-p-dioxin

[2] Cleanup methods, if necessary, will be determined by the laboratory.

[3] "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, 3rd edition, November 1986 and Update I, July 1992.

[4] "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983.

H.2.9.0 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

This section presents the internal quality control checks and the frequency of the checks which will be employed for field measurements and laboratory analyses.

H.2.9.1 FIELD QC

Quality control procedures for field measurements will be limited to checking the reproducibility of the measurements in the field by obtaining multiple readings and by calibrating the instruments (where appropriate).

Quality control of field sampling will involve collecting field duplicates and field blanks in accordance with the applicable procedures and frequencies described in Sections H.2.4.1 and H.2.5.0, and the level of effort indicated in Table H.2.1.

H.2.9.2 LABORATORY QC

Specific procedures related to internal laboratory QC samples (namely, matrix spikes, surrogate spikes, blanks, blind check samples, laboratory duplicate and matrix spike duplicates) are detailed in the following subsections.

The internal QC checks for the analyses will follow the appropriate methods specified in Table H.2.10 and the laboratory SOPs in Attachment H.2-1.

H.2.9.2.1 Initial and Continuing Calibration Checks

The compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of

producing acceptable quantitative data. The initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of an analysis run, while the continuing calibration checks document that the initial calibration is still valid, and that satisfactory maintenance and adjustment of the instrument on a day-to-day basis is achieved. The specific control criteria and corrective action requirements for these calibrations will be as specified in the respective methods presented in Table H.2.10 and the SOPs presented in Attachment H.2-1.

H.2.9.2.2 Internal Standards Performance

The internal standards performance criteria ensure that GC/MS sensitivity and response is stable during every run. Acceptance criteria will be as specified in the referenced methods.

H.2.9.2.3 Method Blank Samples

A method blank sample will be analyzed by the laboratory at a frequency of one blank per twenty analyses or, in the event that an analytical batch consists of less than twenty samples, one method blank sample will be analyzed. The method blank sample, an aliquot of analyte-free water or sodium sulfate for solid organic analyses, will be carried through the entire analytical procedure.

H.2.9.2.4 MS/MSD, MS/DUP

MS/MSD and MS/DUP sample sets will be analyzed at a minimum frequency of one per twenty investigative samples. Acceptance criteria and compounds that will be used for matrix spikes are identified in the SOPs presented in Attachment H.2-1. Percent spike recoveries will be used to evaluate analytical accuracy while relative percent difference between the duplicate analyses will be used to assess analytical precision.

H.2.9.2.5 Surrogates

Surrogates are used in all GC and GC/MS analyses. Every blank, standard, and investigative sample including MS/MSD samples will be spiked with surrogate compounds prior to purging VOC or extracting SVOC and pesticide/PCB samples.

Surrogates will be spiked into the samples according to the appropriate analytical methods. Surrogate spike recoveries will fall within the control limits set by procedures specified in the method for analytes falling within the quantitation limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates out of the quantitation limit; assessment of analytical quality in these cases will be based on the quality control embodied in the calibration check and MS/MSD samples.

H.2.9.2.6 Blind Check Samples

As supplied by IDEM, an analytical batch may contain a blind check sample. In general, the blind check sample will be obtained from IDEM and supplied to CRA. The analytes employed in this check sample will be a representative subset of the analytes of interest.

The percent recovery of analytes will be calculated from the results of the check samples as defined in Section H.2.13.2.

H.2.9.2.7 Trip Blank Samples

Trip blank samples will be submitted with aqueous investigative VOC samples only, and will be used to determine if cross-contamination has occurred during the shipment and storage of investigative samples. Trip blank samples will be prepared by the laboratory by filling two preserved 40-mL vials with organic-free deionized water. The

trip blank samples will be kept with the investigative samples throughout the duration of the sampling event and, upon return to the laboratory, will be analyzed to determine the presence of VOC introduced during shipment and/or storage.

H.2.10.0 DATA REDUCTION, VALIDATION AND REPORTING

HLI will perform analytical data reduction in-house under the direction of the laboratory QA officer. The laboratory QA officer will be responsible for assessing data quality and advising CRA of any data which were qualified based on laboratory QC criteria. Data reduction, review and reporting by the laboratory will be conducted as detailed in the following. It should be noted, however, that "sign-off" will be required following completion of each step.

1. Raw data produced and reduced by the responsible analyst is turned over for independent review by another analyst.

2. The area supervisor reviews the data for attainment of quality control criteria presented in the referenced analytical methods.

3. Upon completion of all reviews and acceptance of the raw data by the laboratory operations manager, a report will be generated and sent to the laboratory quality assurance officer.

4. The laboratory QA officer will complete a thorough inspection of all reports.

5. The QA officer and area supervisor will decide whether any sample re-analysis is required.

6. Upon acceptance of the preliminary reports by the QA officer, final reports will be generated and signed by the QA officer.

CRA QA/QC Officer - Analytical Activities will conduct an evaluation of data reduction and reporting by the laboratory. These evaluations will consider the finished data sheets, field blank data, field duplicate data and recovery data for surrogate and matrix spikes. The material will be checked for legibility, completeness, correctness and the presence of requisite dates, initials, and signatures. The results of these checks will be assessed and reported to the project managers noting any discrepancies

and their effect upon the acceptability of the data. All information garnered for QA/QC checks will be discussed in a Data Quality Assessment and Validation report.

Validation of the analytical data will be performed by the CRA QA/QC Officer - Analytical Activities based on the relevant QC criteria outlined in "Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses", February 1, 1988 and "Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses", October 1989. Assessment of analytical and field data will include checks for data consistency by looking for comparability of duplicate analyses, potential sample contamination as indicated by results of field blank sample analyses, laboratory QA procedures, adherence to accuracy and precision criteria, transmittal errors and anomalously high or low parameter values. The results of these data validations will be reported to the project manager, noting any discrepancy and their effect upon usability of the data.

Raw data from field measurements and sample collection activities that are used in the project reports will be appropriately identified and appended to the report. Where field data have been reduced or summarized, the method of reduction will be documented in the report. In addition, field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

All data packages provided by the laboratory will consist of the following deliverables:

i) a case narrative that includes a summary of analytical methods used and a description of any unusual action or conditions;

ii) dates of sample receipt, extraction/digestion and analysis;

iii) method blank sample summaries;

iv) surrogate compound recovery data and matrix spike/matrix spike duplicate recovery data and control limits (for organics);

v) matrix spike recovery data and duplicate sample analysis data and control limits (for inorganics);

vi) check sample data; and

vii) executed chain-of-custody records.

The data packages will be stored with the evidentiary files as described in Section H.2.6.4.

H.2.11.0 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analyses are performed in accordance with the procedures established in Section H.2.5.0. The audits of field and laboratory activities include two separate independent parts: internal and external audits.

H.2.11.1 FIELD AUDITS

Internal audits of field activities (sampling and measurements) will be conducted by the CRA QA/QC Officer - Field Activities. The audits will include examination of field sampling records, field instrument operating records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures and chain-of-custody. These audits will be conducted to correct deficiencies and to verify that QA procedures are maintained throughout the RI/FS. The audits will involve review of field measurement records, instrumentation calibration records and sample documentation.

Any external audits may be conducted by IDEM, as required.

H.2.11.2 LABORATORY AUDITS

The internal performance and system audits of the laboratory may be conducted by the CRA QA/QC Officer-Analytical Activities. The system audits, which will be conducted as deemed necessary by the CRA project manager or the CRA QA/QC Officer - Analytical Activities, will include examination of laboratory documentation of sample receiving, sample log-in, sample storage, chain-of-custody procedure, sample preparation and analysis and instrument operating records. The performance audits may be conducted on a quarterly basis. Blind QC samples will be prepared and submitted along with project samples to the laboratory for

analysis throughout the project. The QA officer will evaluate the analytical results of these blind performance samples to ensure the laboratory maintains acceptable performance.

Any external audits may be conducted by IDEM, as required.

H.2.12.0 PREVENTIVE MAINTENANCE

All analytical instruments to be used in this project will be serviced by the laboratory personnel at regularly scheduled intervals in accordance with the manufacturer's recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of the laboratory personnel will be performed by the equipment manufacturer or its designated representative.

Daily checks of each instrument will be performed by the analyst who has been assigned responsibility for that instrument. The manufacturer's recommended procedures will be followed in every case. Table H.2.11 presents routine preventive maintenance for laboratory and field instruments.

The pH and conductivity meters will be calibrated in the field as described in the SOPs in Attachment H.2-1. In addition, the following preventive maintenance measures will be taken in the field:

Water Level Tape - Clean probe and lower three feet of tape with Alconox™ detergent wash and deionized water rinse to prevent hard water and iron buildup.

TABLE H.2.11

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES FOUR COUNTY LANDFILL FYULTON COUNTY, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Gas Chromatograph/Mass Spectrometer (GC/MS)	1. Replace pump oil as needed. 2. Change septa weekly or as often as needed. 3. Change gas line dryers as needed. 4. Replace electron multiplier as often as needed. 5. Replace gas jet spliter as needed. 6. Replace GC injector glass liner weekly or as often as needed. 7. Replace GC column as needed. 8. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 9. Check to ensure the pressure on the primary regulator never runs below 100 psi.	1. Syringes 2. Septa 3. Various electronic components 4. Glass jet spliter 5. GC column 6. Glass liner
Gas Chromatograph	1. Change septa weekly or as often as needed. 2. Change gas line dryers as needed. 3. Replace GC injector glass liner weekly or as often as needed. 4. Replace GC column as needed. 5. Clean/replace GC detector as needed. 6. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 7. Check to ensure the pressure on the primary regulator never runs below 100 psi.	1. Syringes 2. Septa 3. Detectors 4. Glass liner 5. GC column

TABLE H.2.11

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES FOUR COUNTY LANDFILL FYULTON COUNTY, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Purge and Trap Sample Concentrator	1. Replace trap as needed. 2. Decontaminate the system after running high concentration samples or as required by blank analysis. 3. Leak check system daily or as often as needed. 4. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 5. Check to ensure the pressure on the primary regulator never runs below 100 psi.	1. Spare traps 2. Spare sparger 3. Various electronic components/ circuits 4. Plumbing supplies - tubing fitting
Graphite Furnace Atomic Spectrophotomer (GFAA)	1. Change graphite tube contact rings as needed. 2. Change D2 background correction lamp. 3. Clean quartz window as necessary. 4. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 5. Check graphite tubes and replace as necessary.	1. Contact rings 2. D2 arc lamp
Mercury Analyzer	1. Clean tubing and quartz cell weekly or as often as needed. 2. Clean aspirator as necessary. 3. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP.	1. Quartz cells 2. Aspirator

TABLE H.2.11

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES FOUR COUNTY LANDFILL FYULTON COUNTY, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Inductively Coupled Plasma Spectrometer (ICP)	1. Clean torch assembly and mixing chamber when discolored or after eight hours of running high dissolved solid samples. 2. Clean nebulizer as needed. 3. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP.	1. Spare torch mixing chambers 2. Spare nebulizer
pH Meter	1. Check battery (if used in field); and replace if discharged. 2. After use in samples containing free oil, wash the electrode in soap and rinse thoroughly with water. Immerse the lower third of the electrode in diluted HCl (1:9) solution for 10 minutes to remove any film formed. Rinse thoroughly with water. 3. Keep electrode properly filled with appropriate filling electrolyte solution.	1. Standard buffers 2. Electrolyte filling solution 3. Spare electrodes
Specific Conductivity	1. Check battery (if used in field); and replace if discharged. 2. After use in samples containing free oil, wash the electrode in soap and rinse thoroughly with water.	1. Standard solution 2. Spare electrodes

H.2.13.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy and completeness achieved during the associated sample analyses.

H.2.13.1 FIELD MEASUREMENTS

Field data will be assessed by the CRA QA/QC Officer - Field Activities for compliance with the established QC criteria that are specified in the QAPP. Accuracy of the field measurements will be assessed using daily instrument calibration, calibration check and analysis of blanks. Precision will be assessed on the basis of reproducibility by duplicate readings of a single sample. Data completeness will be calculated using the following equation:

$$\text{Completeness} = \frac{\text{Valid (usable) Data Obtained}}{\text{Total Data Planned}} \times 100$$

The required level of completeness will be 80 percent.

H.2.13.2 LABORATORY DATA

Laboratory results will be assessed for compliance with the required precision, accuracy, completeness and sensitivity as follows:

H.2.13.2.1 Precision

Precision of laboratory analysis will be assessed by comparing the analytical results of MS/MSD samples for organic analyses and laboratory duplicate analyses for inorganic analyses. The relative percent

difference (%RPD) will be calculated for each pair of duplicate analyses using the formula in Figure H.2.2.

H.2.13.2.2 Accuracy

Accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections H.2.4.0 and H.2.9.0 of the QAPP using the analytical results of method blanks, reagent/preparation blanks, MS/MSD and MS/DUP samples, field blanks and trip blanks. The percent recovery (%R) of matrix spike samples will be calculated using the formula in Figure H.2.2.

H.2.13.2.3 Completeness

Completeness will be assessed by comparing the number of valid (usable) results (as determined by CRA QA/QC Officer - Analytical Activities) to the total possible number of results using the formula presented in Section H.2.13.1. The required level of completeness for laboratory analyses will be 80 percent.

H.2.13.2.4 Sensitivity

The achievement of targeted quantitation limits depend on instrumental sensitivity and matrix effects. Therefore, it is important to monitor the instrumental sensitivity to ensure the data quality through consistent instrument performance. The instrumental sensitivity will be monitored through the analysis of method blanks and calibration check samples.

Equation 1 Determination of Arithmetic Mean ($\bar{X}$)

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where n = number of measurements

X_i = value of measurements

Equation 2 Determination of Standard Deviation (σ_{n-1})

$$\sigma_{n-1} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1}}$$

where n = number of measurements

X_i = value of measurements

$\bar{X}$ = arithmetic mean

Equation 3 Determination of Percent Relative Standard Deviation (% RSD)

$$\% \text{ RSD} = \frac{\sigma_{n-1}}{\bar{X}} \times 100$$

where σ_{n-1} = standard deviation

$\bar{X}$ = arithmetic mean

Equation 4 Determination of Percent Recovery (% R)

$$\% \text{ R} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

where SSR = Spiked Sample Result

SR = Sample Result or Background

SA = Spike Added

Equation 5 Determination of Relative Percent Difference (RPD)

$$\text{RPD} = \left(\frac{|R_1 - R_2|}{\left[\frac{R_1 + R_2}{2}\right]} \right) \times 100$$

where R_1 = value of first result

R_2 = value of second result

figure H.2.2

STATISTICAL FORMULAE
FOUR COUNTY LANDFILL SITE
Fulton County, Indiana

CRA

H.2.13.3 STATISTICAL EVALUATIONS

In the evaluation of data and determination of precision and accuracy, standard statistical formulae will be used.

H.2.13.3.1 Arithmetic Mean

The arithmetic mean is the average obtained by dividing a sum by the number of its addends. A number of recovery results are averaged together to improve the accuracy of the measurement. Figure H.2.2, equation 1 summarizes the formula to be used to determine the arithmetic mean.

H.2.13.3.2 Standard Deviation

The standard deviation is the square root of the average squared difference between the individual values and the average value. A number of recovery results are evaluated to find the numerical variation in the data which is then used in the determination of the percent relative standard deviation. Figure H.2.2, equation 2 summarizes the formula to be used to determine the standard deviation.

H.2.13.3.3 Percent Relative Standard Deviation (%RSD)

The percent relative standard deviation is obtained by dividing the standard deviation of the values by the arithmetic mean of the values and multiplying by 100. The %RSD is calculated on a series of measurements to evaluate an instrument's analytical precision (e.g., initial calibration). Figure H.2.2, equation 3 summarizes the formula to be used to determine %RSD.

H.2.13.3.4 Percent Recovery (%R)

The percent recovery of a parameter is obtained by dividing the amount recovered by the true amount added and multiplying by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. Figure H.2.2, equation 4 summarizes the formula to be used to determine the percent recovery.

H.2.13.3.5 Relative Percent Difference (RPD)

The relative percent difference is obtained by dividing the difference between two numbers by their arithmetic mean and multiplying by 100. The RPD is used to evaluate the analytical precision of two replicate measurements (e.g., matrix spike/matrix spike duplicate). Figure H.2.2, equation 5 summarizes the formula to be used to determine RPD.

H.2.14.0 CORRECTIVE ACTION

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system will be:

1. checking the predetermined limits for data acceptability beyond which corrective action is required;

2. identifying and defining problems;

3. assigning responsibility for investigating the problem;

4. investigating and determining the cause of the problem;

5. determining a corrective action to eliminate the problem (this may include reanalyses or resampling and analyses);

6. assigning and accepting responsibility for implementing the corrective action;

7. implementing the corrective action and evaluating the effectiveness;

8. verifying that the corrective action has eliminated the problem; and

9. documenting the corrective action taken.

For each measurement system, the analyst will be responsible for identifying the need for corrective action and initiating the corrective action procedure. The laboratory supervisor will be responsible for implementing the corrective action and evaluating its effectiveness. The laboratory QA Officer will be responsible for documenting the fact that the corrective action has resolved the problem. The corrective action taken will depend upon the QA/QC criteria that did not meet the necessary criteria, and

may range from qualifying the data to resampling at the Site. All problems requiring corrective action and the corrective action employed to resolve the problem will be reported. Field corrective action will consist of instrument recalibration, replacement of probes or the instruments and will be documented in the field logbook.

H.2.15.0 QUALITY ASSURANCE REPORT TO MANAGEMENT

Management will receive reports on the performance of the measurement system and data quality following each sampling round and at the conclusion of the project.

Minimally, these reports will include:

1. assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;

2. results of system audits; and

3. QA problems, action taken and resolutions.

The CRA QA/QC Officer - Analytical Activities will be responsible within the organizational structure for preparing these reports. The final report for the project will also include a separate QA section which will summarize data quality information contained in the periodic QA/QC reports to management, and details an overall data assessment and validation in accordance with the data quality objectives outlined in this QAPP.

ATTACHMENT H.2-1

STANDARD OPERATING PROCEDCURES (SOP)
FIELD AND LABORATORY INSTRUMENTATION

I.	FIELD SOPs		
	A.	pH/Temperature	SOP No. PHT-CRA-3
	B.	Specific Conductivity	SOP No. SC-CRA-93
II.	LABORATORY SOPs		
	A.	Chain-of-Custody	SOP No. LO-13.0
	B.	Maintenance and Tracking of Sample Custody	SOP No. OP-8.0
	C.	Reagent and Chemical Handling and Standard Solution Preparation	SOP No. O-1.0
	D.	Washing and Storing Glassware and Other Laboratory Equipment	SOP No. O-2.0
	E.	Monitoring, Maintenance and Use of Milli-Q-Water Purification System	SOP No. FA-5.0
	F.	Maintenance and Monitoring of the Central Deionized Water System	SOP No. F-4.0
	G.	Calculations and Significant Figures	SOP No. D-6.0
	H.	Defining QC Reporting Types	SOP No. Q-3.0
	I.	Analytical Standard Operating Procedures and Analyst Training for Analysis of Volatile Organic Compounds by GC/MS	SOP No. MS-5
	J.	Analytical Standard Operating Procedures and Analyst Training for Analysis of Semivolatile Organic Compounds	SOP No. MS-6
	K.	PCB/Pesticide Analysis by GC/ECD	
	L.	Chlorinated Herbicide Analysis by GC/ECD	
	M.	Water Digestion for Analysis by FAA or ICP	SOP No. AM 200
	N.	Aqueous Sample Preparation for Analysis by FAA or ICP	SOP No. AM 201
	O.	Aqueous Sample Preparation for Analysis by GFAA	SOP No. AM 202
	P.	Acid Digestion of Oils for Analysis by FAA, GFAA and ICP	SOP No. AM 203
	Q.	Solid Sample Digestion for Analysis by FAA, GFAA and ICP	SOP No. AM 204
	R.	GFAA Analysis	SOP No. M-10-12.0
	S.	ICP Theory	SOP No. M-10-13.0
	T.	Mercury Sample Preparation for Analysis by CVAA	SOP No. AM 205
	U.	CVAA Mercury Determination in Water and Solid Samples	SOP No. M-10-19.0
	V.	Cyanide Distillation	SOP No. GN-10-16.0
	W.	Cyanides, Amenable to Chlorination	
	X.	Total Cyanide Analysis	
	Y.	pH Determination	SOP No. AM 206

Z. Total Dissolved Solids
AA. Total Suspended Solids
BB. Alkalinity
CC. Chloride Analysis
DD. Chloride Argentemetric
EE. Ammonia Nitrogen Distillation
FF. Nitrogen, Ammonia
GG. Nitrogen, Nitrate-Nitrite Analysis
HH. Sulfate Turbidimetric
II. Biochemical Oxygen Demand
JJ. Chemical Oxygen Demand

SOP No. GN-10-10.0

pH/TEMPERATURE

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Potentiometric

Reference: "Methods for Chemical Analysis of Water and Wastes:", EPA-600/4-79-020, revised March 1983, Method 150.1

Sensitivity: 0.01 pH unit; 0.1 °C

Optimum Range: pH 1.00 to 12.00; temperature 0 to 100 °C

Sample Handling: Determined on site

Reagents and Apparatus:

1. Temperature compensated pH meter, Fisher Scientific Accumet Series 1000 or equivalent;
2. Combination pH electrode;
3. Temperature sensor;
4. pH buffer solutions, pH 4.00, 7.00, and 10.00 (certified buffer solutions);
5. Deionized water in wash bottle.

Calibration:

1. Press On/Off key to turn meter on. If pH indicator in main display area is not on, press pH key to place meter in pH mode.

   Main display will show pH reading. If ATC probe is attached, temperature reading will appear in center display. If meter was previously standardized, buffers used will be shown in lower display.

2. Set pH display resolution by pressing Exp key until desired resolution is shown.

3. Clear current standardization points by pressing Stdz key. Then, within four seconds, press Clear key. Current standardization points will be removed from instrument memory.

6. Recheck calibration with pH 7.00 buffer solution after a minimum of every 10 samples and after the last sample.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be ±0.2 pH units.

   If the results are outside of the control limits, rinse electrodes and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below). If drift is suspected to be the cause of the problem, clean the electrode and recalibrate. If drift is still apparent, replace electrode.

2. Calibration check results must be ±0.10 pH unit of the true value. If the result is outside of ±0.10 pH unit, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in control calibration.

3. All glassware is to be soap and water washed, tap rinsed and deionized water rinsed prior to analyses unless pre-cleaned sample jars are used.

Interferences:

Interferences in pH measurements occur with presence of weak organic and inorganic salts and oil and grease. If oil and grease are visible, note in logbook. Clean electrode with soap and water, followed by 10% HCl and deionized water. Then recalibrate meter before analysis of next sample.

CONDUCTIVITY

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Specific Conductance

Reference: "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, revised March 1983, Method 120.1

Sensitivity: 10 µmhos/cm

Optimum Range: 10-20,000 µmhos/cm

Sample Handling: Determine on site

Reagents and Apparatus:

1. Conductivity meter - Cambridge Scientific Industries Model 301353 or equivalent;
2. Deionized water;
3. Conductivity standard, 1,413 µmhos/cm @ 77 °F (0.01 M KCl).

Notes:

The conductivity meter is factory calibrated. The calibration is checked using a solution of known conductance and recalibrated, if necessary.

Recalibration:

To recalibrate conductance, remove black plug revealing the adjustment potentiometer screw. Add standard solution to cup, discard and refill. Repeat procedure until the digital display indicates the same value twice in a row. Adjust the potentiometer until the digital display indicates the known value of conductance. To increase the digital display reading, turn the adjustment potentiometer screw counterclockwise (clockwise to decrease).

Procedure:

1. Rinse the inside of sample cup with liquid to be measured. (This is especially important if samples with a wide range of conductivity are to be measured.)

2. Fill sample cup.

3. Fill sample cup at least 2/3 full. If the sample is hot boiler water, allow to cool to 160 °F or below.

4. Slide the right hand function switch to "TEMP" and push the "READ" button. If temperature reading is not stable, empty and refill cup several times to bring cup and sample to the same temperature.

5. Read the temperature on the digital display panel and adjust both temperature compensation knobs accordingly.

6. If the approximate conductance is known, slide the left hand range selector switch to the proper range.

   Example: If you expect the sample to be around 2,000 µmhos, slide the left hand selector switch to x 1,000.

7. Slide the right hand function switch to "COND" and push the "READ" button.

8. Multiply the digital display reading by the factor indicated by the position of the left hand range switch to determine conductance.

   Example: A display reading of 1.00 with the left hand range selector switch indicating x 1,000 is:
   1.00 x 1,000 or 1,000 µmhos/cm

   Note: If a single "1" appears on the left hand side of the digital display, the sample conductance is higher than the selected range. Slide the left hand (range) selector switch in one step intervals until a 3 or 4 digit display appears.

   Conversely, if a decimal display appears (such as 0.11) move the range selector switch to the left until a 3 or 4 digit number, 1.00 or larger, appears on the display. This puts the unit in a range affording the best accuracy. Caution: A single "1" always means that the conductance is higher than the selected range.

9. Repeat steps 1 through 8 for remaining samples.

Quality Control:

1. The quality control calibration check standard must be analyzed initially, after a minimum of every 10 samples and after the last sample. If less than 10 samples are analyzed, the calibration standards are still required. The standards must be within ±10 percent of the true value or the

samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the field logbook.

2. Duplicate a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicate values are to be within ±15% of each other. If outside of this range, reanalyze the samples. If still outside the acceptance range, recollect sample and reanalyze. If still out, replace meter.

Chain of Custody

Submitted by:

Approval

Date 9-10-92

PURPOSE: The purpose of this SOP is to provide guidelines for completing a Heritage Laboratories, Inc. Chain of Custody form. A copy of this form accompanies each sampling kit and should be completed by the sampler.

POLICY: It is the policy of Heritage Laboratories, Inc. to have written SOPs for all aspects of sample analysis.

PROCEDURE:

I. Personnel

Sampling personnel are responsible for completion of chain of custody forms. A completed chain of custody form should be in each sample kit returned to the lab.

II. Procedure

An example of Heritage Laboratories, Inc. sample chain of custody form is shown in Figure A. It includes space for sampling information (who, when, where, what program), analyses requested and shipping change of custody information.

Figure A.

TO ENSURE PROPER HANDLING OF SAMPLES PLEASE COMPLETE THIS ENTIRE FORM

HERITAGE LABORATORIES, INC.

I - № 7455

7901 West Morris Street
Indianapolis, Indiana 46231 (317) 243-0811 Fax (317) 486-5095

Co. Name:
Project Name:
Quote No.: PO No.:
ENVIRONMENTAL PROGRAM:
CWA NPDES _____ IWP _____ SLUDGE _____
RCRA MW _____ SW _____ DISPOSAL _____
SDWA _____ CERCLA/SUPERFUND _____ OTHER _____
Sampled by:

Analyses Requested
(Note specific detection limits or methods)

Report To:
Co:
Add:
Attn:
Phone:
Accelerated Turnaround Requested _____
(Subject to Additional Charge)
Result Request by: ___ / ___ / ___
Mo Day Yr
(Date must be Accepted and Approved by Lab.)

Sample ID:	Date:	Time:	Comp	Grab	Sample Description:	Sample Type (Aqueous) DW GW WW Sed. Oil Sludge Other	No. of Containers										Remarks:	EMS Sample No.

Relinquished by (Signature)	Date / Time	Received by (Signature)	Relinquished by (Signature)	Date / Time	Received by (Signature)
	/			/	
Relinquished by (Signature)	Date / Time	Received by (Signature)	Relinquished by (Signature)	Date / Time	Received by (Signature)
	/			/	
Relinquished by (Signature)	Date / Time	Received for Lab by (Signature)	Date / Time	Remarks:	
	/		/		

Distribution: White original to be retained by client. Yellow copy to accompany sample to laboratory. Pink copy to also be retained by client.

A. Company Information

Enter the name and project number of the company performing the sampling in this block. The Heritage Labs quote number should be entered (if available) as well as the samplers' PO number.

Enter the full address of the individual to be sent the report. IF accelerated (or guaranteed) turnaround is desired, fill in the requested date. Accelerated (guaranteed) turnaround is subject to additional charge and must be approved by laboratory personnel BEFORE the samples are logged into the laboratory system.

B. Sampling and Analysis Information

Indicate the environmental program under which the analyses are being performed.

CWA - Clean Water Act
NPDES - National Pollution Discharge Elimination System
RCRA - Resource Conservation and Recovery Act
SDWA - Safe Drinking Water Act
CERCLA/SUPERFUND - Comprehensive Environmental Response, Compensation and Liability Act (EPA Superfund)

The sampling personnel MUST sign in the area designated.

The site sample ID (if used) can be entered in the first column, followed by the date and time sampled and whether the sample was a grab or composite sample. Date and Time sampled are MANDATORY. Grab samples are those taken in series at an individual sampling site whereas composite samples are those where a large volume of sample is collected, composited (if non-aqueous) and transferred into separate sample containers with the appropriate preservative. There is a space for the client sample description. Sampling suffixes can be used to indicate samples to use for QC such as;

DP = Duplicate
FB = Field Blank
TB = Trip Blank
EQ = Equipment Blank
BG = Background

The sample type (matrix) should be indicated in the column provided. Some abbreviations commonly used are;

RW = Residential Well
MW = Monitoring Well
WA = Water, Non-Specific
SW = Surface Water
SD = Sediment (lake, ditch, river)
SL = Sludge
LE = Leachate
SS = Soil Sample
S/S/S = Other "solid" sample
Oil = Any non-aqueous, non-solvent sample

Enter the total number of sample containers for each sample. Enter the type of analysis requested in the cells next to the "No. of Containers" (i.e. VOA, SVOA, Metals, Cr^{+6}, etc.). Indicate the number of containers submitted for each sample (or check the box if containers are being shared between tests) and test in the appropriate box.

The Remarks column is used for other comments such as safety precautions, preliminary (field) screen information or other sample specific information.

C. Custody Information

The bottom of the form is used to track the individuals who transport the samples. The sampler signs off in the first "Relinquished by" box, and the shipping company representative accepts delivery by signing in the first "Received by" box. Additional transfers are tracked by continuing the "Relinquished by" and "Received by" steps. Upon delivery to the laboratory, the "Received for Lab by" and "Date/Time" are completed. Receiving Personnel comments are made in the lower "Remarks" area (i.e. sample integrity, container appearance, etc.).

III. Documentation

The chain of custody is its own documentation. A copy of the form is returned to the client and the original (top) copy filed in the laboratory files.

IV. Appendix

A. Chain of Custody Checklist

A. Chain of Custody Checklist

Before delivering a set of samples, use the following guidelines to review the chain of custody.

1. Is the customers name and address legible?
2. Are there any special bill to or report to addresses?
3. Is the purchase order number listed?
4. Is the Environmental Program indicated?
5. Is rush turnaround requested? Date indicated? Lab OK'd?
6. Are the customer's sample description or ID indicated?
7. Do the descriptions on the sample bottles match those on the chain of custody?
8. Are the Date and Time sampled listed?
9. Does the date and time on the samples match the chain of custody?
10. Are the analyses requested indicated clearly?
11. Are (will) the samples be properly preserved for the indicated analyses?
12. Are there sufficient sample amounts to perform the analyses?

After the chain of custody has been thoroughly reviewed, it is to be signed by the person who performed the sampling (relinquishing) and the sample courier (receiving).

NOTES:

Discrepancies between chain of custody and samples can increase laboratory turnaround time while being resolved.

Corrections must be made by drawing a single line through the incorrect information and writing the correct information in the same (general) area. Corrections must be initialled and dated.

Maintenance and Tracking of Sample Custody

Submitted by: Susan Brotherton

Approval

9-10-92
Date

PURPOSE: This SOP describes the laboratory procedure for internal sample custody tracking and documentation. This documentation is required to prove that a sample was in custody at every step in the analytical procedure as described by EPA as;

- It is in your possession, or
- It is in your view after being in your possession, or
- It was in your possession and you locked it up, or
- It is in a designated secure area (secure areas shall be accessible to authorized personnel only).

This custody documentation is also used as a means of tracking the sample through the analytical procedure.

POLICY: It is the policy of Heritage Laboratories, Inc. to provide adequate documentation of sample custody during all steps in the analytical process.

PROCEDURE:

I. Personnel

All laboratory personnel shall be trained in the proper methods of maintaining and documenting sample custody throughout the analytical procedure. This shall be documented in group training forms.

II. Facilities

The entire laboratory is designated as a secure sample storage area. It is a limited access area and is protected by the facility security system. Samples are placed in the special storage areas after laboratory ID numbers are assigned. Samples, extracts and standards are stored separately. Samples and extracts are stored for 15 days after testing is complete except when a contract requires longer storage.

A. Walk in Refrigerators

The facility has walk in refrigerators for sample storage. Each refrigerator has separate sections for different tests. These refrigerators are locked during non-business hours. Sample Custodians and laboratory supervisory personnel have keys.

B. Department Refrigerators

Some departments have separate refrigerators for storage of samples, standards and sample extracts. These refrigerators are limited access due to the facility security system. Employees return samples to the proper sample storage areas upon completion of the analysis or at the end of the shift.

III. Procedure

The following procedures apply to those samples which require internal custody maintenance, by contract (CLP) or protocol (GLP).

A. Sample Log In Sheet

A form similar to Appendix A. will be used to document sample receipt at the laboratory by the Sample Custodian or Principal Investigator. This can be filled out as received or computer generated and signed after review.

B. Sample Logbook

Each sample storage has one or more sample logbooks which may be project specific. Each time a sample is added to or removed from the storage area, a record is made in the logbook. This record must indicate the analyst, and lab ID and date and time of transfer.

Disposal of the samples will also be documented in this logbook; the date, initials of the analyst and method of disposal will be entered and the remainder of the page "Z'd" out.

If samples are relocated to another storage area, this is indicated as a removal from the original area and the samples are logged into the new area.

C. Analytical Benchsheets

Benchsheets may be used in place of logbooks in areas where it is not convenient (or wise) to use a logbook. Samples are identified on benchsheets by the EMS number as well as the client identifier (when available on the bottle). Bottles or vials containing prepared samples (extracts, leachates, etc.) are identified by the

EMS number and the fraction or associated prep; ACid, Base-Neutral, PCB/Pest, ICP, GFAA, Lachat, etc. (i.e. A225678BN) and stored appropriately for the method. The analyst initials, date and time entered and extract box (or other sample location) will be entered on the benchsheet. The laboratory name and location and description of analytical procedure will appear on all benchsheets.

D. Extract Tracking

Sample extracts (or other prepared sample) will be logged into the extract storage areas in the same manner as logging into the walk in refrigerator, if the information is not on a prep sheet already. When the extract is removed from the storage area for analysis, the analyst initials, date and time removed and reason is entered in the sample/extract logbook or analytical logbook, as appropriate.

E. Analytical (Instrumental) Logbook

The logbook page will contain the analysis type, the instrument ID # and description, the date and analyst initials, the order of analysis, instrument parameters, maintenance and any other information pertinent to documenting the sample trail.

F. Analytical Raw Data

All notebook pages, benchsheets, graphs, computer printouts, chromatograms, GC/MS spectra and other laboratory case related documents will contain the EMS sample number, the client ID number (if available), the date and initials of the analyst and other information pertinent to the contract or protocol.

IV. Documentation

All sample custody tracking will be maintained in logbooks or on benchsheets. Logbooks can be general purpose or project specific. Bench-sheets will be sequentially numbered and stored in a central location (binder) either by project, sample number or analytical run. All logbooks are reviewed periodically by Project Manager and/or Group Leader or their designee. Benchsheets are reviewed before adding to the binder.

IX. Appendix

A. Sample Log In Sheet

B. Example Analytical Benchsheet

C. Laboratory Sample and Document Flow

A. Sample Log-In Sheet

B. Example Analytical Benchsheet

C. Laboratory Sample and Document Flow

ACTIVITY	DOCUMENTS	PERSONNEL
Sample Receipt	Airbills, Chain-of-Custody Records, Sample Receipt Logs, Traffic Reports, Sample Log In Sheet	Sample Custodian/Receiving Personnel
Transfer to Storage	Sample Log book	Sample Custodian
Transfer to Analytical Preparation	Sample Log book, Extraction Bench Sheets	Analyst
Transfer to Storage	Extraction Bench Sheets, Extract Log book	Analyst
Transfer to Analytical Run	Extract Log book, Instrument (Run) Logs, Printouts, Spectra, Etc.	Analyst
Data Review	Spectra, Chromatograms, Analysis Data Sheets, Review Sheet,	Supervisor
Assembly	Inventory Sheets, Data, Reporting Forms	Data Entry/Document Control Officer
Final Report (Results) Review	Certificates of Analysis QA Summary	QA Unit
Data Package Shipping	Shipping/Mail Log	Document Control Officer/Project Manager
Disposal	Sample Log book	Analyst/Sample Custodian

STANDARD OPERATING PROCEDURE FOR
Reagent and Chemical Handling and
Standard Solution Preparation

EMS-Heritage Laboratories, Inc.

Corporate Office
7901 West Morris Street
Indianapolis, Indiana 46231

NOT
DUPLICATE

Document #: SOP-O-1.0

Submitted by: Susan Brotherton
Greg Busch

Title : Senior Scientist
OA Unit

APPROVAL

Laboratory Manager

Date : 7/13/92

Effective date: _____

Original Copy #: _____

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II. DESCRIPTION

This SOP describes proper laboratory chemical handling procedures and specifies the labeling procedure for all chemicals, reagents and mixtures (including stock solutions and secondary dilutions) used in the laboratory. Procedures for handling gases are covered in a separate SOP.

III. PERSONNEL

All laboratory and shipping/receiving personnel will be trained in proper handling and labeling procedures. This will be documented on the group or study training form. The Group Leader of designee is responsible for periodic review of these procedures.

IV. SAFETY

Prior to handling, read labels and material safety data sheets (MSDS) for every chemical used. Standard laboratory safety equipment, lab coat, safety glasses and gloves must be worn in addition to any other precautions listed in MSDS. Make particular note of the following: fire hazard, health hazard, reactivity hazard, protective equipment, disposal storage and first aid. If certain equipment is specified in the MSDS and not available, consult the safety officer before continuing.

- Never use chemicals in containers which are not labeled properly.

- Always add acid to water, never water to acid.

- Never pipet by mouth.

- When in doubt about an element of safety, consult the lab supervisor, safety officer or chemical supplier.

V. PROCEDURE

The term "chemical" used in this section refers to chemicals, reagents, standards, (GLP) test substances and their serial dilutions used in the laboratory.

A. Chemical receiving

The MSDS must be available at the lab before or at the time of accepting delivery of a chemical into the lab. MSDS's included with the shipping container should be in an external envelope so that it can be read and all precautions followed before opening the container.

All chemicals delivered to the lab will be accepted in the shipping and receiving area. The proper personnel is then notified (i.e. Study Manager or Project Manager, Purchasing Agent, etc).

1. For GLP projects, chemicals are delivered (unopened) to the Study Manager or designee. The Study Manager will open the containers and check for damage or leakage. If the containers are whole, the chemicals are logged into the project logbook, with the date received, identification of the compound (CAS number if possible), the purity or concentration, batch or lot number and stability (with expiration date), and approximate amount. Any of this information missing from the container label must be added. A label for date received, date opened and expiration date will be added. Chemicals will be stored in a secure area as per the protocol. Damaged or leaking containers will be handled according to the appropriate SOP.

2. Chemicals delivered to the lab for regular analytical work will be transferred to storage by the Purchasing Agent or designee. The date received is entered into the Purchasing Logbook. Each shipping package containing individual containers will be labeled with the date of receipt. When removed from storage to the lab, each container will be labeled with the date the container was opened, the expiration date, and the label initialled by the analyst and dated.

3. Identification numbers

   For ease and/or confidentiality, the chemical can be assigned and all bottles labeled with a unique laboratory compound (project specific) identification number based on the protocol or contract number (i.e. PROT#-#). This information is logged in the project specific logbook. Solutions and dilutions of this compound will be tracked through this number.

4. Certification Statements

   All manufacturers' certification and traceability statements are maintained in files when these statements are not on the label (i.e. for 1 mL vials of organic standards). These files are maintained by the group using the standards or reagents. The statements will be marked with the date received and the identification of the standards logbook where they are referenced.

5. Damaged Materials

Containers that have been damaged during shipping will be discarded, saving the contents if possible. All appropriate information will be entered on the new bottle, and the sequence of events recorded in the project or group standards logbook. If the contents were unable to be salvaged, the supplier will be notified that the shipment was damaged in transit by the Purchasing Department and the contents disposed of properly by the group involved or returned by the Purchasing Agent.

B. Storage

All chemicals will be stored in a limited access area separate from samples, in a manner consistent with the conditions specified by the manufacturer (in the MSDS), sponsor or protocol. This might be a refrigerator, freezer, or a secure area of the lab. Incompatible chemicals msut be stored separate from one another (refer to MSDS).

Test compounds, reagents and chemicals for a GLP study will be separated from other laboratory chemicals in a locked refrigerator, freezer or cabinet. Access to these chemicals will be to Study Manager, QAU or trained personnel directly involved with the project.

C. Standard solution preparation

Each laboratory group or study must have a standard prep logbook for documenting the preparation of serial dilutions standards. Each entry must contain the name or code number of the chemical or reagent, the weights and volumes used, dilution instructions for use, and the date and initials of the analyst. There must be no handling of the reagents directly from the reagent bottles (unless the entire contents of the container are to be used, or unused portions discarded). Instead, minimal amounts are to be placed in interim holding containers. Stock solutions are to be made from reagent grade chemicals and pesticide grade (or equivalent) solvents. Acids msut be reagent grade. Aqueous dilutions are made with DI or Type II water as appropriate with the method.

Unless outlined under a separate protocol, the following procedure is to be used in the preparation of stock solutions and secondary dilutions.

1. Stock solutions

Stock solutions will be prepared in a clean area (see SOP-GLP-12.0 Low Level Laboratory Policies). The balance will be checked against class "S" weights bracketing the weight range before use. Class "A" glassware or calibrated ependorf pipets are used for all solution prep. At least 0.100 grams or 1.0 mL of reagent is to be used. Materials may be weighed into an intermediate vessel such as a weighing dish, etc., and then transferred into a volumetric flask (rinsing with solvent). Once the solid material is in the volumetric flask, solvent is added to the mark and the flask agitated until the chemical(s) is completely dissolved. All stock solutions are documented in the appropriate group or study logbook.

Stock solutions will be stored in appropriate containers (glass with teflon lined cap, plastic bottle with cap, etc.) and under conditions as specified in MSDS or other manufacturers' documentation.

All bottles will be labeled with the chemical name or ID number, the concentration, the date prepared and analyst initials and expiration date.

2. Secondary (Serial) dilutions

Serial dilutions of the stock standard used in the laboratory will be recorded in the appropriate group or study logbook. Dilutions must be done using Class "A" glassware or calibrated pipets.

Dilutions of stock solutions will be stored in appropriate containers (glass with teflon lined cap, plastic bottle with cap, etc.) and conditions as specified in MSDS or other documentation.

All serial dilutions will be labeled with the compound name or ID number, concentration, dilution date and analyst initials and expiration date.

D. Holding time

1. Expiration dates/QC Limits

Expiration dates will be assigned based on information from MSDS's, manufacturer or supplier and past experience for those chemicals or solutions which have a

finite lifetime.

a. Chemicals with unspecified expiration dates

Chemicals with no expiration date supplied by manufacturer or supplier must be assigned an expiration date. The experience of the analyst, group leader or QAU may be used to determine the most reasonable date the quality of the chemical will remain intact.

For example;

solvents and other liquid reagents-1 year;
solid chemicals-2 years;
solutions-6 months (1 week for volatiles).

Assigned expiration dates must be documented in the standard receipt logbook or standard prep logbook when solutions (or dilutions) are made along with the date, analyst initials and source of the expiration date.

In addition to expiration dates, the QC recovery limits for the standard must be recorded in the logbook or the appropriate method control chart referenced.

2. Extensions

Near or at the expiration date, the analyst can check the integrity of the compound or solution (titration or chromatography, etc) and a new expiration date assigned if appropriate. This shall be documented in the original entry in the appropriate logbook as to the proof of standard integrity (control chart, method recovery, etc), and the date and initials of analyst.

This should only be done if it is more cost effective than making/purchasing and validating a new standard.

E. Contaminated Chemicals

Any chemical suspected to be contaminated must be tested (titrimetrically, chromatographically or other) to determine its purity prior to use. If the chemical is contaminated, it must be disposed of, according to the SOP for Waste and Sample Disposal or GLP protocol.

As in V.D.3, only do this if it is more cost effective than purchasing new standard (or none immediately available) or if

the chemical was used in an analytical sequence under QA audit/question.

F. Disposal

When the compound or solution has reached its expiration date or if it is contaminated, it will be disposed of according to guidelines in the MSDS. See SOP for Sample and Waste Disposal or appropriate method.

VI. Documentation

All receipt, mixing and dilutions of chemicals will be documented in the purchasing, project or group specific logbook. The manufacturers' certification of purity or traceability are stored in the group files until archived. Packing slips are maintained in the Purchasing Department for one year after delivery.

SOP Distribution List

SOP TITLE: Reagent and Chemical Handling

SOP NUMBER: 0-1.0

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STANDARD OPERATING PROCEDURE FOR
Washing and Storing Glassware and Other
Laboratory Equipment

EMS-Heritage Laboratories, Inc.

Corporate Office
7901 West Morris Street
Indianapolis, Indiana 46231

DO NOT
DUPLICATE

Document #: SOP-O-2.0

Submitted by: Susan Brotherton Title : Senior Scientist
Ron Byers Metals Group Trainer
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APPROVAL

Gary A. Kingla Date : 7-14-92

Laboratory Manager

Effective date: _____

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II. DESCRIPTION

This SOP contains the washing procedures for laboratory glassware and other apparatus. The diverse requirements for the wide range of tests and studies within the lab make it necessary to have several different methods. The washing SOP's will be posted at the appropriate sinks in the lab.

III. PERSONNEL

All laboratory personnel will be trained in the apparatus washing procedures pertinent to their group methods. This will be verified on the group or study training form.

IV. SAFETY

Normal safety precautions must be followed when washing equipment. Safety glasses, lab coat and gloves are mandatory. Other safety supplies such as double or special gloves, rubber aprons or face shields are necessary for some procedures (i.e. when handling concentrated acid). Broken glassware must be removed immediately and either disposed of properly or set aside for repair. Broken glassware containers are located in every lab. Handle concentrated acids and organic solvents under a fume hood.

V. PROCEDURES

Unless outlined in a separate SOP, the procedures in Appendices A-C are to be followed for all laboratory equipment.

All glassware must be washed (or set to soak) as soon after use as possible.

All open-ended laboratory glassware must be stored in a drawer when not in use or covered to prevent accidental contamination.

The specific glassware washing procedures are described in Appendices A-C. Do not oven-dry any volumetric glassware, or any piece of glassware with a ground-glass joint. The volumetric ware will be out of specifications in volume, and the ground-glass joints will not connect properly because of expansion.

Glassware should be rinsed with water by filling the container at least half full, swirling it around and dumping the water out. Solvent rinsing is defined as adding enough solvent (water, organic solvent or acid solution) to throughly wet the sides of the container as the container is rotated. Pour the used solvent into appropriate containers for disposal.

Appendix A. General Inorganic Group

A-1. General

All glassware is rinsed with tap water immediately after use. Glassware is washed with micro and hot water, rinsed 2-3 times with hot water and finally twice in DI water.

Pipets are placed in the pipet washer (filled with 50 mL micro + tap water) immediately after use. When the washer is full (after soaking pipets at least 1 hour), the micro/water is drained and the pipets rinsed with 2-3 volumes of DI water. Add 150 mL of conc. HNO_3 to the last full DI rinse and let sit for 1 hour. Rinse with several volumes of DI water and remove pipets to drain. Refill the pipet washer with micro/water.

A-2. Oil and Grease

The oil and grease separatory funnels and other laboratory glassware are washed with micro and hot water, rinsed several times with hot water and finally with DI water. The oil and grease equipment is rinsed with freon immediately before use.

A-3. BOD Glassware

Before use, clean all bottles with a detergent, rinse them thoroughly and then rinse them with "No-Chromix" or chromic acid solution. Pour the acid from bottle to bottle (maximum number of 8 bottles) stopper and swirl. Rinse thoroughly first with tap water and then triple rinse with distilled water and let drain dry. Drain the bottles well (CAUTION: "No-Chromix" and chromic acid are both very corrosive. Extreme care should be taken to avoid contact with skin or clothes.) Dirty BOD bottles will cause errors in the test. Thoroughly rinsing with distilled water is especially important; otherwise the acid left in the bottles will lower the pH and kill the bacteria. Check the rinse water with pH paper.

Appendix B. Metals Group

B-1. General Instructions

Glassware should be rinsed with tap water and placed in a bath of mildly acidic water (2% HNO_3) immediately after use. Rinse the glassware with water and place in a micro/hot water (20 mL micro + 1 liter water) bath. Scrub each piece thoroughly to remove obvious contamination and inspect glassware while rinsing. Remove all soap residue.

Rinse with DI water two times, rinse once with 1+1 HNO_3 and rinse three times with DI water. Place in 1+1 HNO_3 acid bath for one to two hours. Remove glassware from acid bath and rinse three times with DI water. Check pH of rinse water randomly to ensure all acid has been rinsed away.

The acid bath is changed every 2-3 weeks, levels of common metals must be checked on the ICP every week to determine need for change. This is documented in a logbook.

B-2. ICP Waters Glassware

Follow the general instructions in B-1 above.

Keep all ICP water prep glassware separate from other glassware.

Use only ICP designated acid baths. Store all ICP waters glassware in separate drawers.

B-3. Low-Level GFAA Waters Glassware

Follow the general instructions in B-1 above.

Keep all low-level GFAA waters prep glassware separate from all other glassware.

Use only low-level designated acid baths. Store all low-level GFAA waters glassware in GFAA or other labeled drawers.

Final rinse of all low-level GFAA waters glassware should be done with Milli-Q water. Analysts must rinse glassware with 1+1 HNO_3 and Milli-Q water (three times) just prior to use.

B-4. Solids Glassware

Follow general instructions in B-1 above.

Oil flasks should be acetone reinsed immediately after use and soaked in dilute HNO_3 solution (1:20).

B-5. EPTOX, TCLP and Other Large Glassware

Follow general instructions in B-1 above.

Large pieces of glassware (filtering flask, etc) do not need to be soaked in an acid bath. However, be sure to thoroughly rinse with 1+1 HNO_3 followed by two DI water rinses. Do this twice and add one additional DI water rinse the second time.

Oily residue may be removed from glassware with acetone.

Be sure to scrub inside of stems on all funnels and filter holders.

B-5. Mercury Glassware

Rinse bottles with cold tap water immediately following Hg analysis. If bottles will not be washed the next day (i.e. over the weekend), store them "wet" in a 10% HNO_3 solution.

Mark any bottles which contained samples with high concentration of mercury and store in a 50% HNO_3.

Rinse bottles with hot tap water once, cold tap water twice and DI water once. Fill 1 bottle with concentrated HNO_3 for each set of 24 or fewer bottles. Using a glass funnel, slowly pour the concentrated HNO_3 from bottle to bottle. Rotate the bottle while pouring to ensure that entire neck is acid washed. Move through each set of 24 bottles twice with the same HNO_3. Rinse 3 times with DI water.

Appendix C. Organic Groups

C-1. PCB/Pest, Semi-volatile Prep (General Cleaning)

Wash glassware with hot, micro water, scrubbing all surfaces with a brush, being careful not to scratch the glassware with any portions of the brush which may be abrasive. Sonicate small pieces to ensure that all particulate matter is loosened.

Rinse glassware with hot, tap water.

Rinse with deionized water, three times.

Allow to air dry (or rinse with ACS-grade acetone and allow to dry).

Rinse with pesticide-residue grade solvent before use.

Store cleaned glassware in a dust-free environment (or cap with aluminum foil).

Rinse glassware immediately prior to use with the solvent that will be used in the analysis.

Keep all plastics away from the glassware both during and after cleaning to prevent the possibility of phthalate contamination.

C-2. Herbicide

Follow the general instructions above, but after rinsing glassware in hot water, rinse with 1+1 HCl and then three times with DI water. Acetone rinse or air dry. Store covered in labeled drawers. Rinse with pesticide residue grade solvent immediately prior to use.

C-3. Volatile Glassware

Drain the purge vessels.

Add a squirt (~ 1 mL) of Micro detergent and rinse glassware with at least three volumes of hot, tap water or until the foam is gone. Scrub the syringe barrels and plungers with a brush.

Rinse with deionized water, thoroughly.

Re-attach purge vessels to the purge and trap device. Put the syringe parts in a beaker to drain before use.

Keep all solvents away from the glassware to prevent possibility of contamination.

C-4. ZHE Apparatus

* Assume the vessel is filled with sample and buffer and has just come off the agitator. The liquid leachate should have been transferred into a Tedlar bag.

Leave the 3-way valve closed and loosen the piston a few turns to relieve any pressure. Open the 3-way valve. Loosen the four hand knobs and take off the top plate. Rinse with DI water and set aside.

Take out the support screens and glass fiber filter. Discard the filter. Using a smaller brush, wash the support screens on both sides, with warm water and Micro soap. Rinse with DI water three times. Check the pores of the screens by holding them up to the light to see if they are clogged. If they are, the particles can be removed by tapping the screens with a spatula and running high pressure water through them. Sonication in warm, soapy water is also helpful. If the screens are covered with a tar or paint, etc, sonicate the parts in methylene chloride. If any solvent is used for cleaning, be sure to boil the parts in a beaker for several minutes in the prep lab. This will remove the solvent and prevent contamination of the VOA and ZHE prep lab.

Remove the O-ring on top of the cylinder. Wash with soap and water. If the O-ring has an odor to it, try boiling in water for a few minutes. If it has any organic material that does not wash off, rinse with acetone or methylene chloride. (Always be sure to boil the part afterwards). Rinse with DI water.

To separate the cylinder, crank the piston down to the bottom. Then raise the piston approximately half an inch and insert the plastic braces. Lower the piston all the way. Lift off cylinder. Wash the cylinder with soap and water. If there is organic material remaining inside, solvents may be necessary to remove it. Boil (if solvents are used) and rinse with DI water.

Wash the top with a brush and soapy water. Be sure to clean the grooves. Use solvents only if necessary (boil afterwards). When rinsing with DI water, allow some to flow through the valve to flush out any remaining leachate.

The two O-rings must be removed from the piston before cleaning. Clean these O-rings as above. Clean the surface of the piston with a brush, soap and warm water. Use a small brush to clean the grooves where the O-rings were. Again, use solvents if necessary but boil afterwards. Rinse with DI water.

After the vessel is clean, reassemble for use or spread the pieces out to air dry if the vessel is not going to be used that day. If the pieces seem to have an odor to them (but no obvious "dirt"), lay them out on paper towels and let them air out a day or two or boil them and let them air dry.

SOP Distribution List

SOP TITLE: Washing and Storing Glassware and Other Equip

SOP NUMBER: 0-2.0

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Monitoring, Maintenance and Use of Milli-Q Water Purification System

NOT DUPLICATE

Submitted by: Linda Osborn

Approval _____ Date 9/21/92

PURPOSE: This SOP describes the procedures required for the Milli-Q Plus water purification system installed in the Indianapolis facility.

POLICY: It is the policy of Heritage Laboratories, Inc. to have written SOP's for maintenance and use of all laboratory equipment.

PROCEDURE:

I. Personnel

All personnel who use the Milli-Q system must be trained in the operation of the system. The laboratory group leader or designee is responsible for daily monitoring and maintenance.

II. Safety

Standard safety precautions should be taken while using or performing maintenance on the system. This includes wearing safety glasses and lab coats. Make sure to clean up all spills.

III. Equipment and Instrumentation

A. Milli-Q Description

The Milli-Q Plus water system is designed to provide the final polish to water that has been pretreated. In this case, the lab DI water is used as the source water. This system produces water suitable for low level analyses such as inorganic graphite furnace metals and TOC, and organic analyses by GC/ECD, GC/MS and HPLC.

Water passes through four expendable cartridges: a Super-Q, two Ion-Exchange and a final Organex-Q. There is also a final filter unit which removes microorganisms larger than 0.22 microns not removed by the previous filters. The system includes automatic [illegible] pulsation controls to assure that water

quality will not degrade between uses by periodically recycling the water.

The log book for monitoring and maintenance is located in the laboratory near the equipment.

B. Other Equipment

Specific Conductance meter and probe

IV. Chemicals, Reagents and Standards

1.01 N KCl Solution-prepared by the General Inorganic Lab for ASTM-D1125/EPA 120.1.

V. PROCEDURE

A. Monitoring

As with the regular DI water system, the quality of the water is monitored each workday in each group. Samples prepared with water that is found to be out of control are re-prepared and analyzed. The specific conductance of the Milli-Q water is checked daily (workdays) and the system taken out of service, if the conductivity is greater than 1. The specific conductance procedure is described in Appendix A.

B. Maintenance

The feed water quality will determine how frequently the cartridges become exhausted and the product water requirements will determine how often the cartridges should be replaced. The following guidelines will help to decide when cartridges need replacing.

The cartridge replacement procedure is described in Appendix B.

1. Milligard Prefilter Cartridge

This cartridge should be replaced when there is a 0.7 kg/cm (10 psi) pressure drop, as indicated by the gauge between the first and second cartridge housing heads. (Normal Reading with new cartridge = 20 to 30 psi).

2. Super-Q Carbon Cartridge

This cartridge does not directly affect resistivity levels, but should be replaced at the same time as the other cartridges. If organic removal capacity is exhausted,

fouling and shorter life of Ion-Ex cartridges.

3. Ion-Ex Deionizer Cartridges

Replace when the resistivity drops below 10 megohm.cm (0.100 micromho/cm).

4. Organex-Q Cartridge

Replace when the organics level in the product water increases to an unsatisfactory level, based on the application. Replace whenever the Ion-Ex cartridges are replaced.

5. Final Filter Unit

The final filter unit should be replaced when the flow rate decreases to approximately 0.5 Lpm. The final filter should be replaced at least two to four times per year.

C. Use

These instructions are posted near the unit.

1. Turn switch to operate mode.

2. Check to make sure LED reads 18 megohms. Notify the Group Leader immediately if less than 18.

3. Remove cap from the nozzle.

4. Place container under spout. Never use any plastic material if water is to be used for organics.)

5. Turn white handle to "PRODUCT".

6. Fill container to desired level.

7. Turn white handle to "RECIRCULATE" when finished.

8. Replace cap under spout.

9. Turn power switch to standby.

VI. DOCUMENTATION

All maintenance and daily conductance checks are recorded in the logbook. Daily volume use is not recorded.

VII. Appendix

A. Specific Conductance Procedure for Milli-Q Water

B. Cartridge Replacement Procedure

C. Cleaning and Sanitization Procedure

Appendix A. Specific Conductance Procedure for Milli-Q Water

1. Drain 500 mL of Milli-Q water through system.
2. Fill a plastic cup with Milli-Q water.
3. Rinse specific conductance probe with DI water.
4. Put probe into Milli-Q water and record conductance.
5. Measure the temperature of the water and the conductance of the 0.1 N KCl solution.
6. Record KCl conductance and Milli-Q conductance in Milli-Q log with date and initials.
7. If conductance is greater than 1 umhos/cm, the group leader is notified immediately and an out-of control notification form is distributed. The system is flagged as non-usable until maintenance is performed and the conductance lowered to "in-control" levels.

Temperature vs Conductivity, 0.01 N KCl Solution

Temperature (°C)	Conductivity absolute umhos/cm)
15	1141.5
16	1167.5
17	1193.6
18	1219.9
19	1246.4
20	1273.0
21	1299.7
22	1326.6
23	1353.6
24	1380.9
25	1408.1
26	1435.6
27	1463.2
28	1490.9
29	1518.7
30	1546.7

Appendix B. Cartridge Replacement Procedure

Refer to the operator's manual OM-154.

1. Close the feed water supply valve, turn off the pump and open the 3-way valve to relieve internal pressure.

2. Remove the housing bowls and cartridges.

3. Disconnect the final filter unit from the system by removing the tubing from the tube connector on the 3-way valve. Remove the tubing and connector from the filter and discard the filter unit.

4. Install and flush new cartridges using the cartridge installation procedure for your system (Section II of the manual).

Appendix C. System Cleaning and Sanitization

This could potentially introduce contaminents and should only be done if there has been a severe problem or slime is detected. Check with the Group Leader or Chief Chemist before proceeding.

System Cleaning

The insides of the bowls and heads should be thoroughly cleaned each time the cartridges are replaced. Wash the inner surface with a non-abrasive detergent, using a sponge or soft cloth. Rinse several times with clean water to remove detergent residues.

Sanitization

The entire system should be sanitized if slime deposits are detected in the bowl when cartridges are replaced.

1. Remove all of the bowls and cartridges.
2. Discard the cartridges and thoroughly clean the bowls and heads.
3. Replace all but one bowl, without installing cartridges.
4. Place 35 mL of a 5.25% solution of chlorine bleach in the remaining empty bowl and reinstall the bowl.
5. Open the feed water supply and the 3-way valve.
6. Start the pump.
7. When water begins to flow from the outlet, close the 3-way valve and recirculate water for ten minutes.
8. Turn off the pump, close the feed water supply valve, and allow the system to stand idle for at least one hour.

The water remaining in the system at this point should have a chlorine level of approximately 200 ppm.

9. Remove the bowls, carefully and discard the contents. Reinstall the bowls without cartridges.

10. Restart the pump and recirculate water for two minutes.

11. Open the 3-way valve and flush for approximately five minutes (longer, if necessary) to remove all of the residual chlorine.

12. Using a chlorine test kit, (such as the Hach Test Kit), measure the chlorine level in the flush water. Install new cartridges and proceed with normal operation only when the chlorine level is less than 0.1 ppm.

SOP Distribution List

SOP TITLE: Monitoring, Maintenance and Use of Milli Q System

SOP NUMBER: F-5.0

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STANDARD OPERATING PROCEDURE FOR
Maintenance and Monitoring of the
Central Deionized Water System

Indianapolis Location

EMS-Heritage Laboratories, Inc.

Corporate Office
7901 West Morris Street
Indianapolis, Indiana 46231

Document #: SOP-F-4.0

Submitted by: Susan Brotherton Title : Senior Scientist

APPROVAL

_____ Date : _____

Laboratory Manager

Effective date: _____

Original Copy #: _____

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II. DESCRIPTION

This SOP describes the DI water system at EMS-Heritage Laboratories, Inc, in Indianapolis, as well as the procedures for monitoring and maintaining the system.

III. PERSONNEL

All laboratory personnel are trained in the proper testing procedures for monitoring the DI water for their tests.

IV. FACILITIES

The EMS-Heritage Laboratory DI water system uses a centralized series of 5 tanks (activated carbon, cation exchange, anion exchange and two mixed-bed ion exchange) to remove chlorine, salts and organic compounds present in city water. There are two performance indicating meters on the system, one before the last bed and one after. This system is monitored by the receiving personnel. Maintenance of the system is performed by an appropriate wter purification company (i.e. Ionpure Technologies Corporation, Indianapolis, Indiana).

There is an additional charcoal filter on the DI lines in the mass spec VOA lab to remove compounds (dichlorobenzenes, trichlorobenzenes and naphthalene) remaining after this initial treatment. This is necessary for low level volatile organic analyses. This water is monitored by the mass spec volatiles group and maintained by the water purification company.

A Milli-Q water system is used to make ASTM Type II water from the DI water. This water is used in the metals, general inorganics, general organics, semi-volatile and PCB/Pest prep groups and is monitored and maintained by the general organics group. This system is described in the SOP for Monitoring and Maintenance of the Milli-Q Water Purification System.

All plumbing parts (connectors, fittings, tubing, valves, etc) downstream from the purification system are teflon, type 316 stainless steel or PVC tygon. No solvent welded pipe is allowed. All pipe connections must be threaded with teflon tape or teflon pipe dope. No secondary inlets are allowed. All sink fixtures must be rated for DI water.

V. EQUIPMENT AND INSTRUMENTATION

The water is monitored in each lab group as appropriate for the tests. The tests used include:

- In-Line Conductivity Monitoring at the tanks
- General Inorganic Specific Conductance ASTM D1125/EPA 120.1
- Mass Spec Volatile Organic test
- Milli-Q in-line Resistivity Meter

All equipment and instrumentation have an SOP for maintenance and operation as well as a system for tracking the information (logbook or benchsheets).

VI. PROCEDURE

The procedures followed by the laboratory groups differ due to the nature of the tests performed and the quality of water required. Samples prepared with water that is found to be out of control are re-prepared and re-analyzed, if necessary.

The central DI water system is monitored by the receiving personnel. The meter ahead of the fifth tank is checked daily and the conductivity from the last meter recorded in a logbook. When the red light on the first meter is lit, the laboratory personnel are informed and maintenance requested. Response time is generally less than 24 hours, enough time before the last tank can break through (water quality remains acceptable). Maintenance involves replacing the cation and anion exchange tanks, replacing the first mixed bed tank with the second and adding a new mixed-bed tank to the fifth position. The activated carbon tank is replaced semi-annually.

The Specific Conductance of the DI water is measured weekly (or once per analysis sequence) following the SOP for Specific Conductance-ASTM D1125 or EPA Method 120.1 (SOP GN-1). If the conductance is greater than 2 µmhos/cm, the QA Unit, Lab Management and Receiving personnel are notified. The Specific Conductance test is shut down until water quality is restored. All other tests in the lab monitor the water quality in the test using reagent blanks. If these fail, samples prepared with DI water in that sequence are flagged and re-run (if necessary).

The water used for volatile organic analyses is monitored daily in the blank analysis on each volatile organic analysis instrument. When di- and tri-chlorobenzenes appear in the blank (still below the method detection limit), the maintenance company is called to replace the charcoal filter.

The Milli-Q system is described in detail in the SOP for Monitoring and Maintenance of the Milli-Q Water Purification System.

VII. DOCUMENTATION

The conductivity of the DI system is checked daily and the results entered into the Sample Receiving logbook. Benchsheets from the general laboratory Specific Conductance test are archived with other raw data. Logbooks are kept for replacement of filters on the volatiles water lines and on replacement of filters on the Milli-Q system.

STANDARD OPERATING PROCEDURE FOR
Calculations and Significant Figures

EMS-Heritage Laboratories, Inc.

Corporate Office
7901 West Morris Street
Indianapolis, Indiana 46231

Document #: SOP-D-5.0

Submitted by: Greg Busch Title : Director, Quality Assurance Unit

APPROVAL

Laboratory Manager Date : 5/1/92

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II. DESCRIPTION

A key to successful completion of valid and documentable analytical results is consistency in calculating and reporting. This SOP defines formulas used to calculate analytical results.

Reporting analytical results is specified in methods along with method specific QC calculations (i.e. startup QC). Calculations for instrument specific performance criteria (i.e. peak width, column efficiency, resolution, detector sensitivity/efficiency) are detailed in the appropriate instrument SOP.

III. PERSONNEL

It is management's responsibility to make available at the bench level, the Comprehensive QA Plan and it is the group leaders' and analysts' responsibility to know and to follow its requirements. In addition to the QA Plan, pertinent EMS-Heritage SOPs, EMS-Heritage written methods and published (EPA, etc) methods, the analysts must be fully aware and have easy access to any specific contract requirements and Data Quality Objectives (DQOs).

All analysts will be instructed on the correct manner to calculate and report results by their group leader or designee. This will be documented on training forms.

IV. Calculations

A. QC Definitions

1. Accuracy

Accuracy is defined as the ability to achieve the "correct" or true value in an analysis. The accuracy of a test can be measured at several points in the procedure. It is used in startup QC in several methods.

$$Accuracy = \frac{A}{B} \times 100\%$$

Where: A = Average Recovery (of Several Tests)
B = True Value (Reference)

The % Recovery of a standard is often used as a measure of calibration accuracy (i.e. ICV). It can also be used to calculate the recovery of an LCS or known EPA QC standard.

$$\% \text{ Recovery of Standard} = \frac{A}{B} \times 100\%$$

Where: A = Value Measured (Observed)
B = True Value (Reference)

The % Recovery of a spiked sample, SPI or DPS is used as a measure of method efficiency.

$$\% \text{ Recovery of Spike} = \frac{SSR - SR}{SA} \times 100\%$$

Where: SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

2. Precision

Precision is defined as the ability to reproduce a measurement. Replicability within a method is expressed as Relative Percent Difference (RPD). RPDs are used to measure precision between duplicated analyses.

The following formula is used when sample precision is evaluated utilizing matrix spikes (MS) and matrix spike duplicates (MSD).

$$RPD = \frac{2|MSR - MSDR|}{MSR + MSDR} \times 100\%$$

Where: MSR = Matrix Spike Recovery (%R)
MSRD = Matrix Spike Duplicate Recovery (%R)

The following formula is used when sample precision is evaluated from duplicate (unspiked) sample results.

$$RPD = \frac{2|S - D|}{S + D} \times 100\%$$

Where: S = Sample Original Measured Value

D = Duplicate Sample Measured Value

I. Standard Deviation

Standard deviation is used as a measure of the variation in a group of values (i.e. response factors in an initial calibration). It is usually calculated using a calculator or computer. The two common equations for standard deviation are:

$$S = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1}}$$

and

$$S = \sqrt{\frac{\sum x_i^2 - \frac{\sum x_i^2}{n}}{n-1}}$$

Where: $\bar{X}$ = Average of all data points
X_i = Each individual data point

The equation used on any computer or calculator is documented in the operators' manual.

4. Relative Standard Deviation (RSD)

Relative Standard Deviation is the ratio of the standard deviation of a set of numbers to their average, expressed as a percent. It relates standard deviation (or precision of a set of data) to the size of the numbers and is sometimes referred to as the coefficient of variation (CV). This is often used as a measure of initial calibration precision.

$$CV = RSD(percent) = \frac{S}{\bar{X}} \times 100\%$$

$\bar{X}$ = Average

5. Percent Difference (%D)

Some methods require this calculation to compare initial and continuing calibration response factors as a means of determining the validity of the calibration.

$$\% \ Difference = \frac{\overline{RRF_i} - RRF_c}{\overline{RRF_i}} \times 100\%$$

Where: $\overline{RRF_i}$ = Average (relative) response factor from initial calibration

RRF_c = (Relative) response factor from continuing calibration

B. Calculations

1. Equations

Linear equations are used mainly in the inorganic groups. In this method, an equation for a straight line is generated describing the correlation between an analyte concentration (or mass) and an instrument response (absorbance, transmittance, etc.). The formula for a line is

$$Y = mX + b$$

Where: Y = Point on the Y axis (response)
X = Point on the X axis (concentration)
m = Slope of the line
b = y-intercept (x = zero)

This equation is usually generated by a calculator or computer but b and m can be calculated manually using the least squares estimate. This equation can be used if the correlation coefficient (the measure of the match of the data points) is greater than 0.995. It is valid over the calibration range and must be verified throughout the analysis sequence (type and acceptance criteria specified in the methods).

$$m = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sum X^2 - \frac{(\sum X)^2}{n}}$$

$$b = \bar{Y} - m\bar{X}$$

Refer to the method and calculator manual for the correct order for entering the information and calculating the result. The calculated result has the same units as the concentration of the calibration points. The final concentration must be corrected for any prep and/or dilution made.

Other non-linear equations may be used to relate the response of an analyte to the concentration. These must be approved in advance by the QA Department and recorded in the analytical folder.

2. External standards

The external standard method is used mainly by the CC Groups. In this method, the ratio of instrument response to analyte concentration is used to calculate a calibration factor (CF) or response factor (RF).

The average calibration factor ($\overline{CF}$) or response factor ($\overline{RF}$) can be used in place of a calibration curve when the %RSD of the response factors is within method specified limits over the working (calibration) range. This value is valid only over that concentration range and must be verified frequently during the analysis sequence (type and acceptance criteria specified in the method).

$$Calibration\ Factor\ (CF) = \frac{Total\ Area\ of\ Peak\ *}{Mass\ Injected\ (nanograms)}$$

$$Response\ Factor\ (RF) = \frac{Mass\ Injected\ (nanograms)}{Total\ Area\ of\ Peak}$$

* For multi-response pesticides, PCBs, gasolines, diesel, etc., use the total area (or height) of all peaks used for quantitation (except for CLP-OLM01). The units are (area (height) units)/mass.

The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the average calibration or response factor from the calibration performed at the beginning of the analytical sequence. Calibration factors from a calibration check standard can be used if it meets method criteria (%RSD, %Rec etc.).

The concentration of a specific analyte in an aqueous sample is calculated as follows:

$$Concentration\ (uG/L) = \frac{(A_s)\ (V_t)\ (D)}{(V_i)\ (V_s)\ (CF)}$$

Where:
- A_s = Response for the analyte
- V_i = Volume of extract injected, in uL
- D = Dilution factor, if dilution was made on the sample prior to analysis
- V_t = Volume of total extract, in uL

V_s = Volume of sample extracted, in mL
CF = Calibration Factor

If the injection volume is constant, the factor V_i can be omitted.

If a response factor is used, the equation is:

$$Concentration\ (uG/L) = \frac{(A_s)\ (V_t)\ (D)}{(V_i)\ (V_s)} \times (RF)$$

For non-aqueous samples the equation is:

$$Concentration\ (uG/kG) = \frac{(A_s)\ (V_t)\ (D)}{(V_i)\ (W)\ (CF)}$$

or:

$$Concentration\ (uG/kG) = \frac{(A_s)\ (V_t)\ (D)}{(V_i)\ (W)} \times (RF)$$

Where: W = The weight of sample extracted or purged, in grams. Wet or dry weight may be used, depending upon the specific applications of the data.

3. Internal standards

The internal standard method is used mainly by the GC/MS group. A compound similar to target compounds (usually deuterated target compound) is added to each extract and the responses of target compounds are compared. With the internal standard calibration technique, the average relative response factor ($\overline{RRF}$) can be used in place of a calibration curve when the %RSD is within method limits over the working (calibration) range and is valid only over that concentration range. The $\overline{RRF}$ is verified at the beginning of the analysis sequence and the values from that check standard are used to calculate concentrations within that analysis sequence

$$RRF = \frac{A_s}{A_{is}} \times \frac{C_{is}}{C_s}$$

Where: A_s = Response for the standard analyte
A_{is}= Response for the internal standard
C_{is}= Concentration of internal standard
C_s = Concentration of the standard analyte

Response can be the area or height, of a total or extracted ion chromatogram as long as it is consistent with the initial calibration.

In this method, the retention times of the analytes are often compared to that of the internal standard, the relative retention time (RRT), requirements are specified in the method.

$$RRT = \frac{RT_s}{RT_{is}}$$

Where: RT_s = Retention Time of standard analyte
RT_{is}= Retention Time of internal standard

The concentration of a specific analyte in an aqueous sample is calculated as follows:

$$Concentration\ (uG/L) = \frac{(A_s)\ (C_{is})\ (V_t)\ (D)}{(A_{is})\ (V_s)\ (RF)}$$

Where: A_s = Response for the analyte
A_{is}= Response for the internal standard
C_{is}= Concentration of internal standard
D = Dilution factor, if dilution was made on the sample prior to analysis
V_t = Volume of total extract, in mL
V_s = Volume of sample extracted, in L

For non-aqueous samples, the equation is:

For non-aqueous samples, the equation is:

$$Concentration\ (uG/L) = \frac{(A_s)\ (C_{is})\ (V_t)\ (D)}{(A_{is})\ (W_s)\ (RF)}$$

Where: W_s = Weight of sample extracted, in kg

C. Significant Figures

The following rule will be used for the number of significant figures to use in calculations:

For all mathematical operations (addition, subtraction, multiplication, division and exponentiation), retain two more places of figures than will be present in the reported value (computer calculations will use all figures). Drop the rest. No rounding of calculated values or intermediate results should be done until the final value is obtained. No rule can be given for the number of significant places to be retained in final values, however, most tests will be reported to two significant figures and most QC samples will be reported to three significant figures.

Percent recovery (%R) data will be rounded and reported to include the first decimal place unless otherwise specified by the method (i.e. 138.2%).

Relative percent difference (RPD) calculations will be performed using the above rounded % Recovery result when hand calculated, or will use all digits carried by a computer when calculated by computer. The RPD result will be reported to two significant figures (i.e. 11 or 2.3).

Organic methods (GC, GC/MS) require reporting of %RSD and Percent Difference (%D) to the second decimal place.

D. Rounding

The rounding procedure to be followed is:

1. If the figure following those to be retained is less than 5, the figure is dropped and the retained figures are kept unchanged. (i.e. 11.444 is rounded to 11.44)

2. If the figure following those to be retained is greater than 5, the figure is dropped and the last retained figure is raised by 1. (i.e. 11.446 is rounded to 11.45)

3. If the figure following those to be retained is equal to 5, and if there are no figures other than zeroes beyond the five, the figure 5 is dropped and the last-place figure retained is increased by one <u>if</u> it is an odd number or kept unchanged if an even number. (i.e. 11.435 is rounded to 11.44, while 11.425 is rounded to 11.42)

Calculations using Percent Recovery (%R of spikes, etc) or observed result from the RPD calculation will use the rounded (reported) value in the calculation, so that reported %R and final results used in calculations (vs. using un-rounded numbers not found on final reports) will arrive at the same result.

STANDARD OPERATING PROCEDURE FOR
Defining QC Reporting Types

EMS-Heritage Laboratories, Inc.

Corporate Office
7901 West Morris Street
Indianapolis, Indiana 46231

Document #: SOP-Q-3.0

Submitted by: Greg Busch Title : QA Unit

APPROVAL

_____ Date : _____

Laboratory Manager

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II. DESCRIPTION

This document defines the QC types used to report data in prep or instrumental analytical sequences at EMS-Heritage Laboratories. It is also the means for standardizing the use of QC types throughout the laboratory.

III. PERSONNEL

All personnel involved in the analysis, calculation and reporting of analytical data must be aware of the QA requirements of their specific tests. It is the group leader's (or their designee) responsibility to ensure that the correct QC is scheduled in each run (and appropriate spaces labeled on the benchsheets). It is the QA Officer's responsibility to inform the laboratory personnel when new QC types are created and to regularly meet with lab personnel to review QC types and their use. The MIS group is responsible for designing a system to report the QC correctly.

IV. METHODS AND QA/QC REQUIREMENTS

There is one major distinction in the computer definition of QC types, those that refer to a preparation step and those that don't. Preparation is defined <u>for this purpose only,</u> as whether a prep run exists in the computer, not whether a prep was actually performed. (A computer limitation; if a QC type is defined as an "02" and no prep run is available, the QC can not be reported on the final report.) Therefore, medium level volatiles, TKN and lab filtered metals analyses, etc are considered as non-prepped (even though an intermediate step exists between receipt and analysis) by this definition. Each QC type fits into a prep or instrumental "run" as required by the specific SOP for the method. The QC types in use are:

A. Non-prepped

1. Instrument QC

- CAL(01) Initial Calibration

Calibrations standards (the number and frequency of which are specified in each method) are used to establish an analytical curve for that analyte based on absorbance, emission intensity, area or other type of measurable response for known standards. Calibration concentration, observed value and % recovery are reported.

- ICV(01) Initial Calibration Verification

Used to verify the validity of a calibration using standards made from a different source than the initial calibration stock. Report calibration concentration, observed value and % recovery.

- CCV Continuing Calibration verification

Analytical standard that is analyzed to verify that an initial calibration is still valid. The CCV may be from the same source as the initial calibration standards. All sequences (runs) must end with a CCV unless not required by the method. Report calibration concentration, observed value and % recovery.

- CDL01 Contract Detection Limit Standard

A reagent sample to verify that analytes are quantifiable at the detection limit stated. In general, twice the analyte detection limit is a good concentration for the CDL. Frequency of analysis is specified in the methods. Report calibration concentration, observed value and % recovery.

- BLA01 Calibration or Instrument Blank

The BLA01 is an aliquot of DI water containing the same reagents as the sample. This sample is used as the calibration zero for those methods which require it. It also serves as an instrument blank. Report observed value.

2. Analytical QC

- BLA01 Calibration or Instrument Blank

See above.

- DUP01 Sample (QC) Duplicate

For samples not requiring digestion/extraction/etc, a homogeneous, representative aliquot is split and carried through the analytical steps to quantitation. Also used when duplicating a sample (splitting) after prep. Report RPD.

- SPI01 Matrix Spike

An aliquot of homogeneous sample is fortified with a known quantity of specific compound(s) and carried through the analysis and quantitation steps. Report sample concentration, spike concentration, observed value and % recovery.

- DPS01 Matrix Spike Duplicate

The sample is split and spiked with exactly the same amount of analyte as the SPI01. Report same information as SPI01, adding % difference, and the QC sample of the SPI01 as well as the original sample number.

- LCS01 Laboratory Control Sample (Laboratory Fortified Blank)

Control sample of known analyte concentration analyzed by exactly the same method as the samples. Matrix Specific. Report spike concentration, observed value and % recovery.

- DLCS1 Duplicate Laboratory Control Sample (Duplicate Laboratory Fortified Blank)

Spiked exactly as LCS01. Report same information as LCS01 adding % difference, and the QC number of the LCS01.

B. Prepped

- BLA02 Reagent (Method) Blank

BLA02 is matrix specific and is carried through the complete sample preparation (same glassware, reagents etc, as samples). Report same information as BLA01.

- ICV02 Calibration Check (only applicable if the initial calibration was prep'd)

A control sample used to verify the initial calibration curve, when the initial calibration standards are prep'd. Very rare.

- DUP02 Sample (QC) Duplicate

Same as DUP01 but split before any required preparation and carried through to quantitation exactly as the sample. Report same information as DUP01.

- SPI02 Matrix Spike

Same as SPI01 but split before any required preparation and carried through to quantitation exactly as the sample. Report same information as SPI01.

- DPS02 Matrix Spike Duplicate

Same as DPS01 but the sample is split as representatively as possible, spiked and carried through the preparation step(s). Report same information as DPS01.

- LCS Laboratory Control Sample (Laboratory Fortified Blank)

Same as LCS01, but prep'd. Report same information as LCS01.

- DLCS Duplicate Laboratory Control Sample (Duplicate Laboratory Fortified Blank)

Same as DLCS1 but prep'd. Report same information as DLCS1.

V. DOCUMENTATION

This SOP serves the purpose of documenting the QC types used in the lab. Any changes will be documented in a revision of this SOP.

ANALYTICAL STANDARD OPERATING PROCEDURES

AND ANALYST TRAINING

FOR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

BY GC/MS

THIS IS AN EXACT
THE ORIGINAL DOCUMENT

EMS-HERITAGE, INDIANAPOLIS, INDIANA

9/90

MS-5

CONFIDENTIAL

SOP Correction FORM

Heritage Laboratories, Inc

SOP Number: MS-5

SOP Title: Analytical Standard Operating Procedures and Analyst Training for Analysis of Volatile Organic Compounds by GC/MS

Page #: 1, 2, 3, 5, 6, 7, 8, 17,

Requested by : Anne Bradburn Date: 1/5/94

Correction: delete all references to 8240 and replace with 8240A

delete all references to 5030 and replace with 5030A

Reason (if applicable):

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager Signature: Gary A. Klingfa Date: 1/6/94

100892

EMS Test Codes;

0502.3 EPA Method 624
0509.3 Appendix IX Volatile Organics, RCRA
0510.3 SW-846 8240 (RCRA)
SW-846-8260 (Capillary RCRA)-next test to start
0510.9 SW-846 8240 Heated Purge and Trap
0513.3 TCLP Volatile Organics, TC list
0516.3 Drinking Water GC/MS 524.1
0516.5 Drinking Water GC/MS 524.2-in process
0516.9 Drinking Water (8 regulated compounds only)
0522.3 TCLP, Landban Volatiles
0530.1 IDEM RCRA/CERCLA Volatile Organics
0902.0 CLP Volatile Organics

Tuning and Calibration Summary

Each system used for the analysis of volatile compounds must be tuned to meet the abundance criteria listed below for BFB.

Mass	Target value 624/8240	524
50	15%-40%	15%-40%
75	30%-60%	30%-80%
95	100%	100%
96	5%-9%	5%-9%
173	< 2% of 174	< 2% of 174
174	> 50%	> 50%
175	5%-9% of 174	5%-9% of 174
176	95%-101% of 174	95%-101% of 174
177	5%-9% of 176	5%-9% of 176

These criteria can not (usually) be met on any of the instruments using the AUTOTUNE file (APEIO#). It is necessary to adjust the various lenses using MSCAL-Manual Tune. Run PARM RAMP and use the graphics cursor to modify the lens setpoint. The ratios of 69/219/502 should be around 100%/40%/4% for the MS's and 100%/25%-30%/2% on the MSD's. Run mass axis and width calibration and look at a profile scan before storing the tune and exiting the program.

The mass spectrometers are considered to be in tuning compliance for 12 hours after the injection (and passing the criteria) of the tuning compound for SW846 methods and for 8 hours for EPA 524. EPA method 624 has no time limitation on the tune or continuing calibration check, but sequences are not run for greater than 18 hours (due to the sample capacity limitation of the Tekmar purge and trap). Any analytical run which lasts longer than the method allows must include a tune check at or before the time period expires. Background correction may only be used to eliminate column bleed or instrument background ions. A hardcopy report of each tune check (spectrum and mass listing) is kept in the run folder. Background correction technique will be recorded.

The GC/MS systems must be initially calibrated at a minimum of 5 concentrations (for 524 and 8240) to determine the linearity of response. Standards for SW846 methods are run at 20, 50, 100, 150 and 200 uG/L, for EPA 524 are 2, 5, 10, 20 and 50, and for EPA Method 624 are 20, 50 and 100 ug/L (will have to change to 10, 50 and 100 as suggested in the method). Surrogates are calibrated in the same manner as target compounds.

The internal standards and surrogates in use are;

	INTERNAL STANDARDS	SURROGATES
EPA-624 and 8240		
	Bromochloromethane	d4-1,2-Dichloroethane
	1,4-Difluorobenzene	d8-Toluene
	d5-Chlorobenzene	Bromofluorobenzene
SDWA-524.2		
	2-Fluorobenzene	d4-1,2-Dichloroethane
	d4-1,2-Dichlorobenzene	d8-Toluene
		Bromofluorobenzene

Relative response factors are calculated as follows:

$$RRF = \frac{\text{area (compound)}}{\text{area (ISTD)}} \times \frac{\text{concentration (ISTD)}}{\text{concentration (compound)}}$$

The percent standard deviation (% RSD) of the RRF's for each compound are also calculated and reported in the final calibration report (computer generated CBRPT). Each method has initial calibration requirements; for 524, %RSD must be less than 20% or a calibration curve must be used, for 624, %RSD must be less that 35% or a calibration curve must be used, and for 8240, the % RSD of a few compounds (CCC's) must be less than 30%.

Only after the continuing calibration criteria are met are the systems ready for sample analysis. The daily calibration check criteria will be discussed with each method (along with greater detail on the initial calibration). The concentration of analytes in the samples is calculated by;

$$CONC = \frac{\text{RF (sample)}}{\text{RRF (Cal Std)}} \times \text{CONC (ISTD)} \times \text{Dilution Factor}$$

Every sample will be spiked with the appropriate surrogate compounds. The compounds and recovery limits (determined by the average of thirty or more analyses and updated regularly) are:

	WATER		SOIL
	624	8240	low/medium
d4-1,2-dichloroethane	76-114	76-114	70-121
d8-Toluene	88-110	88-110	81-117
Bromofluorobenzene	86-115	76-114	74-121
	ZHE	SDWA *	8260
d4-1,2-dichloroethane	81-145	80-120	**
d8-Toluene	84-106	80-120	88-110
Bromofluorobenzene	95-119	80-120	76-114

* Specified by the method, for drinking water only. Other matrices being analyzed for low level organics will have recovery limits determined.

** Being determined. Since this is not one of the recommended surrogates, there are no method recovery limits.

The volatile surrogate is added to the sample (or diluted sample) before purging.

If any volatile surrogate is outside the accepted range, the sample will be re-analyzed. Both analyses will be reported, for clients who will pay, if the problem persists. All other clients' reports will contain the note "Sample re-analyzed with no improvement in surrogate recovery".

A DI spike and matrix spike and matrix spike duplicate will be performed as directed in the method. The compounds used and the limits are discussed in the individual methods. The recovery of the spike compounds are determined by the formula:

$$\% \text{ Recovery} = \frac{(\text{Conc in spiked sample} - \text{conc in sample})}{\text{Spike concentration}} \times 100\%$$

The relative % difference (% RPD) is calculated for recoveries of each compound in the spike and spike duplicate. The formula is:

$$RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-recovery in spike D2-recovery in spike duplicate

BLANK ANALYSES

A method blank will be run once per each analytical run. The concentration of target compounds must be below the detection limit except for common lab solvents (acetone, methylene chloride, methyl ethyl ketone, toluene, freon) which can be 5 times the detection limit. A holding blank will be analyzed regularly.

Any target compound present in the blank, above the detection level will be reported. If samples must be analyzed with a poor blank (due to holding times or RUSH), any sample containing a similar amount of the compound (outside the acceptable range) will be reported, the results flagged and the sample re-analyzed when the source of the contamination is identified and removed.

VOLATILE ANALYSIS BY PURGE AND TRAP GC/MS

ANALYSIS SUMMARY-In the purge and trap analysis, a 5 mL aqueous sample (or dilution of soil extract) is purged with helium bubbles which strip the volatile compounds out of the sample. The helium flows through a Tenax/silica gel/charcoal trap where the compounds are adsorbed. Larger sample volumes and/or heating the sample can be used to achieve a lower detection limit. After the purge cycle is complete, the trap is quickly heated (desorb preheat) and the flow of helium is reversed through the trap while the temperature remains elevated. During this step, the compounds are deposited on the GC column. The GC oven is heated and compounds are separated on a 1% SP 1000 on Carbopack B column or a 105 meter Restek fused silica capillary column and pass through the jet separator to the mass spectrometer. The trap is baked out further before cooling to purge the next sample. The mass spec scans for ions with masses between 33-300 amu. Identification is made by comparing the mass spectra and retention times of sample peaks to reference spectra and retention times in a data base. Reference spectra are obtained from analysis of calibration standards under the same conditions used for analysis. Quantitation is performed using the internal standard method, comparing the response of the quantitation ion of the compound to the ion of the compound used as the internal standard. Surrogates are added to all analyses.

Method 524.2 is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products.

Method 624 is used to determine and quantitate volatile organic compounds present in municipal and industrial discharge (NPDES permits). The report for 0502.3 contains the NPDES compounds (in the order they appear on the permit).

Method SW846-8240 is used to determine volatile organic compounds in a variety of solid waste matrices as well as liquid samples. The report for 0510.3 contains the 624 analytes plus compounds on the Hazardous Substance List and some common solvents, in alphabetic order. This is not the complete list of compounds with the potential of being analyzed by this method. Clients often request additional analytes which require calibration, when possible.

Up to 10 additional compounds identified in the samples are also reported except for regulatory tests such as Appendix IX, and TCLP CCWE and TC lists. Quantitation is also available for clients who require it.

The method detection limit is 5 uG/L (0.32 mG/kG in medium soils) for most of the analytes, others with low volatility or poor ionization are reported with a detection limit of 25 uG/L (1.6 mG/kG in soils). Using the heated purge and trap for low level soil analysis, a detection limit of 5 uG/KG is reported. Purging 25 mL of water decreases the detection

limit by a factor of 5. All detection limits are corrected for sample dilution or variance from the method in the prep. The analyte lists with detection limits are included in Appendix I (report cover sheet).

The holding time for preserved water and soil samples is 14 days from the date of collection until analysis for 524, 624 and 8240 and 10 days from date of receipt for CLP samples.

QC SUMMARY

All methods require an initial demonstration of laboratory accuracy and precision. Analyze five to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration from 1 to 5 times the detection level. Calculate the measured concentration of each analyte, the mean concentration and mean accuracy (mean percentage of true value) and the precision (RSD) of the measurements. This is used to determine the MDL for the method and is also used as a training procedure to assure that the analyst can meet the precision and accuracy requirements of the analysis. All analysts must meet these criteria before starting a (new) analysis.

The system must meet BFB criteria before starting the volatile analysis sequence for initial calibration or daily sample analysis.

After the system has met the BFB criteria, a continuing calibration standard containing method target compounds is purged and analyzed to ensure that the method criteria are met.

A method blank is run before any sample analyses are done to assure that the system/instrument background is under control.

After these criteria have been met, sample analysis can begin.

STANDARD PREPARATION

STORE ALL STANDARDS AND SURROGATE SOLUTIONS IN THE FREEZER. ENTER ALL STANDARDS AND RECORD THE NUMBER OF THE INDIVIDUAL MIXES IN THE LOG BOOK AND THE LOT # WHEN A NEW VIAL IS OPENED. All pertinent information regarding the dilution of standards must be entered into the log book, in detail at least once (in the front of the logbook), and referred to each time a standard is made. Include the type of standard (524, 624, 8240, STD, ISTD, Surr), new standard number, analyst initials and date, and dilution instructions.

Standards are purchased from Supelco, Chem Service or Restek. All the CLP compounds (used to calibrate the RCRA and 624 tests) are present in four Supelco solutions; Purgeable Standards A, B, and C (200 uG/mL) and Volatile TCL-1 mix (2000 uG/mL). Restek provides four 2000 uG/mL and one 5000 uG/mL standards that include the same compounds (plus a second Xylene). The Chem Service HSL mix contains the same compounds as TCL-1 at a concentration of 200 uG/mL.

To make the stock calibration check standard from Supelco standards, use 100 uL of the A, B, C and 10 uL of TCL-1 (or 100 uL of HSL in place of TCL-1) to 1 mL in methanol (final concentration in solution 20 uG/mL). (Ten uL of the 2000 uG/mL Restek plus 4 uL of the 5000 to 1 mL in methanol gives the same 20 uG/mL stock standard.) This solution usually lasts 2-3 days.

The 524 standards are purchased in 6 mixtures from Supelco, each at a concentration of 2000 uG/mL. To make the stock solution, dilute 50 uL of each solution to 1 mL in methanol (concentration of 100 uG/mL), and then dilute 100 uL of this intermediate to 1 mL in methanol (final concentration 10 uG/mL).

The internal standard/surrogate solution for all methods, is made by adding 50 uL of Supelco's internal standard solution (1000 ug/mL) and 200 uL of the surrogate mix (250 uG/mL) to 2 mL of methanol (final concentration 25 uG/mL ISTD and surrogates).

The BFB tune check solution is made by diluting the neat compound in methanol. The stock standard is diluted in water for purging or directly injected on the GC column to check the tune.

Initial calibration standards

Separate ISTD and surrogate solutions are needed for initial calibration since the surrogates must be calibrated at all concentrations. The ISTD solution is made by diluting 50 uL of the Supelco mix (1000 uG/mL) to 2 mL of methanol (25 uG/mL). The separate surrogate solution is made by adding 200 uL of the 250 uG/mL solution to 2 mL of methanol (25 uG/mL).

EPA Method 524.2 is calibrated at 2, 5, 10, 20 and 50 uG/L. The initial calibration solutions are made by adding 5, 12.5, 25, 50 and 125 uL of 10 uG/L stock plus 2, 5, 10, 20 and 50 uL of surrogates (25 uG/mL) are added to 25 mL for these standards. 5 uL of the stock (25 uG/mL) ISTD only is

added to each standard (ISTD Concentration = 5 uG/L).

EPA Method 624 is calibrated at 20, 50 and 100 uG/L. The initial calibration solutions are made by adding 5 uL, 12.5 uL and 25 uL of the standard 20 uG/mL and 4, 10 and 20 uL of the 25 uG/mL surrogate 20 uG/mL initial calibration stock solutions to 5 mL of DI water. 6 uL of the ISTD only (25 uG/mL) are added to each syringe (ISTD Concentration = 30 uG/L). (This will be changed to 5 uL in 10 mL and use only 5 mL in order to run a 10 uG/L standard as stated in the method.)

The 8240 initial calibration solutions are made by adding 5 uL, 12.5 uL, 25 uL, 37.5 uL and 50 uL of the standard (20 uG/mL stock) and 4, 10, 20, 30 and 40 uL of surrogate 25 uG/mL initial calibration stock solutions to 5 mL of DI water for 20, 50, 100, 150 and 200 uG/L standards. Add 10 uL of the ISTD only stock to each syringe (ISTD Concentration = 50 uG/L).

(This would be so much easier if the initial cal surrogate was diluted 160 uL to 2 mL for a concentration of 20 uG/mL. Then the same volume of the standard stock and surrogate could be added.)

Daily calibration standards

The daily 524 standard is made by diluting 25 uL of the 10 uG/mL stock and 5 uL of the ISTD/surrogate in 25 mL of water for 10 uG/L of target compounds and 5 uG/L ISTD/surrogate.

The daily 624 standard is made by diluting 5 mL of the 20 uG/mL stock 6 mL of the ISTD/surrogate mix in 5 mL for 20 uG/L of target compounds and 30 uG/L of ISTD/surrogate.

The daily 8240 standard is made by diluting 12.5 uL of the 20 uG/mL stock and 10 uL of the ISTD/surrogate stock in 5 mL for a 50 uG/L standard.

TEKMAR PURGE AND TRAP OPERATING PROCEDURES

LSC 2 With 10 Place Autosampler.

These systems are the older models used in the lab. The purge and trap is independent and can only be activated when it is in "desorb ready" by a signal from the GC (not the computer).

Front Panel

POWER — Main Power switch, push on/off, illuminated.

TRACE — Power to valve and line heaters, push on/off, illuminated.

DRAIN — Manual drain of sampler, operates in any mode, push on/off, illuminated.

SELECTOR SWITCH — Nine position switch selects the information to be displayed on the digital temperature readout (°C).

SP1 — Temperature of the trap above which system will not advance from STANDBY to PURGE READY, variable 0° to 90° C. For normal use, this is set to 30°; during prepurge, it is set to 90° so the trap temp will not slow down the prepurge cycle.

SP2 — Temperature of GC oven (external thermocouple) above which system will not advance from PURGE COMPLETE to DESORB READY, variable 0° to 180° C. Set to 50°.

SP3 — Trap DESORB PREHEAT temperature, variable 0° to 180° C. Set point 175°.

SP4 — Trap DESORB temperature, variable 50° to 240° C. Set point 180°.

SP5 — Trap BAKE temperature, variable 160° to 340° C. Set point 220°.

T1 — Trap actual temperature.

T2 — GC oven (external thermocouple) temperature.

T3 — Six port valve temperature.

Auto — Displays T2 in PURGE COMPLETE and DESORB READY modes, displays T1 at all other times.

AUTO/HOLD/ STEP

Auto — Automatically steps from step to step.

Hold — Locks system in any of the eight operational steps.

Used to keep the purge and trap on desorb ready for the GC activate.

Step Spring loaded position manually advances through the operational steps one at a time.

X1, X.1 Changes range of DESORB timer from 0-99 to 0-9.9 minutes.

DIGITAL CLOCK READOUT Displays elapsed time in each of the three timed steps (PURGE, DESORB, BAKE).

DIGITAL TIME SELECTORS 0-99 minutes digital thumbwheel switches select total time for each timed step.

PROGRAM DECISION SWITCHES START Pushbutton starts PURGE Mode manually.

AUTO/HOLD In AUTO, the system will proceed directly from DESORB READY to DESORB PREHEAT. In HOLD, the system requires external permission (e.g. GC ready signal or manual override) to advance.

AUTO/RESET In AUTO, the system proceeds with BAKE mode. In RESET, BAKE mode is bypassed to STANDBY.

PURGE PRESSURE Pressure regulator establishes desired gas pressure (max. 20 psig).

PURGE FLOW Precision needle valve for control of purge gas flow rate.

DRY PURGE OPTION On/Off Power switch enables (disables) dry purge mode.

Timer Dial set timer to desired wet purge time. Total purge on front panel should be wet + dry purge time.

Purge Time The purge time should be chosen so as to achieve good sensitivity and reproducibility. Times longer than 15 minutes generally have few benefits, and can lead to breakthrough of the trap. The purge time is usually set at 11 minutes. The dry purge time (when used) should be around 4 minutes.

Purge Flow Rate The purge flow rate is normally 40 mL/min. Faster flow rates can affect trapping efficiency of the low molecular weight compounds such as chloromethane. Lower flow rates reduce the purging efficiency of the higher molecular weight compounds such as bromoform.

Desorb Time A desorb time of 4 minutes works well for flow rates from 0.5 to 50 mL/min.

Bake Time The bake time is usually 7 (to 10) minutes. For heavily load[illegible] [illegible]ntaminated) longer times (up to 20 minutes) may be required. Raising the temperatures do not increase the bake efficiency and can lead to shorter adsorbent lifetimes.

Because the samples analyzed often contain compounds which do not completely desorb, and the air is often contaminated with solvents from the prep areas, the purge vessels are usually prepurged to completely clean out the system before sample analysis. Baking out each position daily is not usually necessary and will decrease the lifetime of the trap. If there has been a highly contaminated sample, baking out that position (and the next, if there was carryover) is all that is needed.

Prepurge

Wash all the purge vessels in hot soapy water and rinse several times with DI water. Shake out as much water as possible and attach to the ALS. Insert purge line into each vessel and make sure that the valve is closed. Reset the purge ready temperature so that the system doesn't wait for equilibrium. The temperature is set to the highest temperature possible for SP1, 90°C. The purge time is set to 4 minutes, desorb to 0 minutes (don't want any of the nasty stuff to go on the column) and bake to 3 minutes. Switch from "hold" to "auto", set the "last sample" dial, press the "first cycle" button and hit the start button. The system will go by itself until the entire system has been prepurged.

Reset the purge ready temp to 30° and switch from auto to hold before starting analysis.

LSC 200 and ALS 2016

The most important thing to remember about the LSC 2000 is that if the 5890 GC is ready, even if there is no run set up by the computer, and the Tekmar gets to desorb ready, it will automatically advance to desorb. The LSC 2000 advances on the "ready" signal not on a "start run" signal from the GC. The other difference is that the LSC 2000 allows the bake flow to bypass the purge vessel, lessening the possibility of carryover from highly contaminated samples.

There is capability to store 4 methods on the LSC 2000. Method 1 is programmed for sample analysis, 2 for prepurge, etc. Read the manual for complete instructions on programming the instrument, the theory is the same as for the LSC2. The soft keys on the front panel F1-F4, are used to advance through the programming software. They correspond directly to commands found on the bottom line of the LCD screen. The "ALS" function is used to program the sequence of the run/prepurge. Set the first and last sample position. (If more than one method is required, set the enable method schedule on both the ALS and Sched screens to Y.)

Call up the correct method for prepurge. (The first page of the Method startup sequence allows the setting of the temperatures.) All temps, except for the mount temp are set to 100°. The mount temp is set to

slightly above room temp. For prepurge, the trap temp is set to 90°. The system stays in "standby" until all temperatures have equilibrated. When all the parameters have reached the setpoints, the green light on the program panel advances from standby to purge ready and a different screen appears. This screen prompts you to press START to begin the prepurge cycle. Do it!!

Change to the correct method for sample analysis (one with the trap temp at <30°).

STANDARD OPERATING PROCEDURES FOR INSTRUMENT LOGBOOKS

The instrument identification must be labeled on the front and include the dates covered. The inside cover must contain the names of the BAMON, TUNE, METHOD, IDFILE, CAL FILE, the name and initials of the analyst and group leader. The GC conditions for tune check and analysis, including the column used and temperature programming need to be listed also. The initials of the "logbook police" must also be listed at the top of a page for logbook review dates, errors identified, etc. (These may be added to the back of logbooks presently in use.) Logbooks should be reviewed regularly.

Sample runs must be entered into the instrument log book. Include sample (Tekmar) position, EMS #, dilution factor (if any), file name and time samples removed from the storage area. Also refer to the GC METHOD and BEDIT files used. All log book entries must be initialled and dated at the bottom of the list, the analyst initials must be labeled "analyst".

Method 524.2

The initial demonstration of laboratory accuracy must be performed before samples can be analyzed. The method validation requires that seven 2 uG/L standards be analyzed and the mean and standard deviation calculated. The mean accuracy should be 80%-120% as calculated by

$$\frac{\text{average recovery}}{\text{spike concentration}} \times 100\%$$

and the RSD should be less than 20%. Some analytes, particularly the early eluting gases and late eluting higher molecular weight compounds are measured with less accuracy and precision than other analytes (although no specific guidelines are given).

The method detection limits are calculated by analysis and quantitation of seven 1 uG/L standards (or the mean of the seven 2 uG/L could have been used). The detection limit is calculated by multiplying the standard deviation of each analyte result by 3.1427. The method detection limits must be sufficient to detect analytes at the required levels. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte.

Initial calibration- The BFB tune criteria (25 nG on column) must be met before calibration can take place. EPA Method 524.2 is calibrated at 2, 5, 10, 20 and 50 uG/L. ISTD concentration is 5 uG/L . The chromatogram of the 10 uG/L standard should be checked for;

1. GC performance- the peaks should be symmetrical with minimum tailing, and

2. MS sensitivity- the GC/MS/DS peak identification software should be able to recognize an analyte in the appropriate retention time window for each compound and make correct tentative identifications. If fewer that 99% of the compounds are recognized, system/software maintenance is required.

After these performance criteria are met, the rest of the calibration standards may be analyzed. The % RSD of the response factors must be less than 20 % or a calibration curve may be generated.

Control charts are suggested in the method to chart the performance of analyte and surrogate measurements as a function of time. Until the mainframe LIMS computer can/will do this, a folder containing copies of the recovery of spikes and surrogates will be maintained. Variations of this data as well as internal standard and surrogate area over time will be monitored and corrective action taken when required (if areas fall to <50% from the initial calibration). Recoveries of the regulated eight compounds and surrogates will be manually charted until the mainframe is ready.

Daily calibration-The MS tune must be verified at the beginning of each 8 hour shift. A medium concentration (10 uG/L) standard is then analyzed

under the same MS conditions. The areas of internal standards a surrogates in continuing calibration checks should not be less than 30 % greater than 50% from the most recent continuing calibration.

The response factors must be within 30% of the initial calibration as reported in CBCHK. If these criteria are met, then the analysis continues with the analysis of a method blank. If the calibration does not pass for a few non-regulated compounds, but analysis is required for priority RUSH or holding times, at the discretion of the analyst and group leader, analysis can proceed with the analyte(s) in question flagged if present in samples and re-analyzed when the system is in control. Sample concentrations are calculated using the daily calibration response factors.

A spiked blank can be used in place of a method blank <u>BUT</u> the recoveries of everything must be within 80%-120% (suggestion - do both!). (A spiked blank (spiked at 5 uG/L) must be analyzed every 20 samples.)

There should be no regulated target compound in the blank above the detection limit. If a non-regulated compound does appear in the blank, it is up to the discretion of the analyst/group leader as to whether to accept the blank or re-analyze it. (The chromatograms take so long to analyze, running another BFB and standard are almost necessary to get any samples done). If an analyte appears in a sample which was in the blank, it will be reported (flagging the results) and re-run when the blank problem is under control.

Analyze samples. Set up the sequence so that the (estimated) inject time of the last sample is within 8 hours of the time the BFB passed.

<u>Additional QC</u>- A low level (2 uG/L) standard should be analyzed weekly to prove the detection limits can be met.

At least quarterly, replicates of laboratory fortified blanks (spiked and duplicate spike DI water) should be analyzed to determine the precision of the lab.

At least quarterly, analyze a quality control sample from an external source.

Sample matrix effects have not been observed when this method, therefore matrix spikes are not required. It is recommended that sample matrix effects be evaluated at least quarterly using the external source standard.

Method 624

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the initial startup as follows. The method validation step requires that four 20 uG/L standards be analyzed. The mean and standard deviation of the calculated results are calculated. These values must meet the method criteria as listed in TABLE 5 of the method. The procedure must be repeated for those analytes which fail these criteria.

The method detection limits are determined from the analysis of seven 5 uG/L standards, quantitated as usual. The mean and standard deviation are calculated and the MDL determined by multiplying the standard deviation (of the seven analysis) by 3.1427.

Initial calibration- The BFB tune criteria (50 nG on column) must be met before calibration can take place. EPA Method 624 is calibrated at 20, 50 and 100 uG/L. The ISTD concentration is 30 uG/L. The RSD for all compounds must be less than 35%.

Daily calibration-The MS tune must be verified at the start of each analytical sequence. A 20 uG/L daily calibration standard is analyzed and the results compared with the "Q" values in Table 5. If the standard passes, then the method blank is analyzed. If the calibration does not pass for a few compounds, but analysis is required for priority RUSH or holding times, at the discretion of the analyst and group leader, analysis can proceed with the analyte(s) in question flagged if present in samples and re-analyzed when the system is in control. Alternatively, a new three point calibration can be generated for that (those) compound(s).

No target compounds should be in the blank above the detection limit (except for common solvents which can be 5 times the detection limit). If a compound does appear in the blank, it is up to the discretion of the analyst/group leader as to whether to accept the blank or re-analyze it. If an analyte appears in a sample which was in the blank, it will be reported (flagging the results) and re-run when the blank problem is under control.

Analyze samples. There is no time limit for analysis so load the sampler as full as possible, emptying the vessels and prepurging as the sequence goes on to add further samples (make sure the BEDIT file is full enough).

Required QC-A minimum of 5% of the samples (per matrix) must be spiked with all analytes (at 10 uG/L), the results compared with %P in Table 5 and reported. Spiked blanks should be analyzed once per 20 samples and the results compared to "P", but the frequency can be decreased if the sample spike recoveries regularly pass the criteria. The control limits for surrogates and spike recoveries are set from the analysis of 30 or more analyses as the mean ± 2 standard deviations for the warning limit and mean ± 3 standard deviations for the control limit. These values are updated quarterly.

Method 624 Table 5

	Range for "Q" uG/L	Limit for S.D. uG/L	Range for Mean uG/L	Range for P %
Benzene	12.3-27.2	6.9	15.2-26.0	37-151
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
Chloroethane	7.6-32.4	11.4	8.4-40.4	14-230
2-Chloroethylvinyl-ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
Bromodichloromethane	13.1-26.9	6.4	10.1-26.0	35-155
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.5	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethylbenzene	11.8-28.2	7.5	17.4-26.7	37-162
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Chloromethane	D-40.8	19.8	D-45.9	D-273
Methylene Chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-162
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.5	54-156
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.6-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl Chloride	0.8-39.2	20.0	D-43.5	D-251

Method 8240/8260

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the initial startup as follows. The method validation step requires that four 20 uG/L standards be analyzed. The mean and standard deviation of the calculated results are calculated. These values must meet the method criteria as listed in TABLE 5 of the EPA 624 method. The procedure must be repeated for those analytes which fail.

The method detection limits are determined from the analysis of seven 5 uG/L standards, quantitated as usual. The mean and standard deviation are calculated and the MDL determined by multiplying the standard deviation (of the seven analysis) by 3.1427.

Initial calibration- The BFB tune criteria (50 nG on column) must be met before calibration can take place. SW8246-8240/8260 is calibrated at 10, 20, 50, 150 and 100 uG/L. The ISTD concentration is 50 uG/L. The RSD must be less than 30% for those compounds identified as Calibration Check Compounds (CCC's). In addition the response factors must be greater than 0.3 for the compounds designated as System Performance Check Compounds (SPCC's).

Volatile CCC's	Volatile SPCC's
1,1-Dichloroethene	Chloromethane
Chloroform	1,1-Dichloroethane
1,2-Dichloropropane	Bromoform (0.25)
Toluene	1,1,2,2-Tetrachloroethane
Ethylbenzene	Chlorobenzene
Vinyl chloride	

Daily calibration-The MS tune (50 nG of BFB on column) must be verified at the start of each analytical sequence. A 50 uG/L calibration check is analyzed. The response factors of the SPCC's must meet the same criteria as for the initial calibration and the %RSD for the CCC's must be less than 25%. While there are no criteria on the rest of the compounds, be alert that all compounds (especially ketones and 1,1,2,2-Tetrachloroethane) have an area high enough to maintain the detection limit. If the retention time for any internal standard changes by more than 30 seconds, or the area of the internal standard changes by more than a factor of 2 (-50% to +100%) from the last calibration check, the system must be inspected for malfunctions and repaired. If the standard passes, then the method blank is analyzed. If the calibration does not pass for a few compounds, but analysis is required for priority RUSH or holding times, at the discretion of the analyst and group leader, analysis can proceed with the analyte(s) in question flagged if present in samples and re-analyzed when the system is in control.

No target compounds should be in the blank above the detection limit (except for common solvents which can be 5 times the detection limit). If a compound does appear in the blank, it is up to the discretion of the

analyst/group leader as to whether to accept the blank or re-analyze if. If an analyte appears in a sample which was in the blank, it will be reported (flagging the results) and re-run when the blank problem is under control.

Analyze samples. Set up the sequence so that the (estimated) injection time of the last sample is within 12 hours of the time the BFB passed.

Required QC-A minimum of 5% of the samples (per matrix) must be spiked and duplicate spiked with the CLP analytes (at 50 uG/L for water and 50 uG/kG) and the % recoveries and RPD values compared with those in CLP. Spiked blanks should be analyzed once per 20 samples and the results compared to the same criteria, but the frequency can be decreased if the sample spike recoveries pass the criteria. Recovery criteria are being developed for TCLP (ZHE) samples, which are spiked with each target compounds on the basis of the original waste stream.

CLP MS/MSD Recovery Criteria

	Water		Soil	
COMPOUND	RPD	REC.	RPD	REC.
1,1-Dichloroethene	14	61-145	22	59-172
Trichloroethene	14	71-120	24	62-137
Benzene	11	76-127	21	66-142
Toluene	13	76-125	21	59-139
Chlorobenzene	13	75-130	21	60-133

The control limits for surrogates and spike recoveries are set from the analysis of more than 30 analysis as the mean ± 2 standard deviations for the warning limit and mean ± 3 standard deviations for the control limit. The values for aqueous and soil matrices should, if applicable, meet the limits established by EPA-CLP. Other matrices (i.e. ZHE) can be calculated and used without comparing to these values. These limits are updated quarterly.

The area of internal standards must not vary more than a factor of 2 or the sample must be re-analyzed. If the surrogate recovery does not pass, check the areas and calculations, and re-analyze the sample, diluting if necessary OR flag the results as estimated concentration.

Preparing Samples- EPA Method 624, SW846-5030

Make sure that the sample number and identification/client on the sample container matches the description on the LIMS work list.

Prepare samples as follows;

1. Water samples-Fill syringe with sample, adjust to 5 mL and load the autosampler. Make sure that the valve is turned in the correction direction. Dilution is often necessary, if you can smell solvents, dilute 1:10 (or 1:100). Do not use volumes less than 10 uL in diluting samples.

   Add ISTD-surrogate to each syringe.

2. Solid samples (medium level 624/8240) - Weigh out 2 grams of a solid an oil into 4.5 mL of methanol. Add 0.5 mL of surrogate solution (0.5 mL to 10 mL of Supelco stock = 12.5 uG/mL) so the concentration of surrogate in the sample is 1.25 uG/mL. Draw off one autosampler vial and cap for FID screening and fill a 1.5 mL screw-cap vial for volatiles analysis. Dilute 200 uL of the methanol solution to 5 mL of DI water (the concentration of surrogate is 50 uG/L) and add 10 uL of initial calibration ISTD solution. Dilute further if FID screening shows high concentration of compounds.

   For ultimate detection limits, use the heated purge and trap with 5 grams of soil. Add the ISTD/Surrogate solution in 5 mL of water (just like a method blank). If the sample smells, be careful. Even though the client may want the lowest detection limits, the sample matrix may prevent it.

SEQUENCE FILE

Use BEDIT to update the sequence file with the correct sample description and FRN. Make a hard copy of the file (BLIST) to include in the run folder. Make sure that the files are consecutive and the Quant output file number matches the Data file number. Check that there are no duplicate file names and that the Quant file will be stored on the correct CRN (NOT AQ).

A typical printout will look like this:

Sequence File: V624::N1

```
Tune File: MTEI01            (Manual Tune File-MS#1)

CR List: D3,D2,L2            (CRN to store the data)
CR Cut-off: 200 blocks                (Minimum amount of room on a disc
                                      required before starting an analysis)

                                       Report Data Archive
                                      Quant : : ID Archive
Number of samples:     15    Sample Size : : : : Output Archive
                                Bottle : : : : : :
Samp Data File      Sample Name        : : : : : : :   Quant ID
 No. Method File    Misc Data          : : : : : : :   Quant Output
001) >90243         A213990          00 1 Y N Y N Y    ID624
     VOLP                             Dil=1.000      ^90243::L2
```

Etc.
The data from this analysis will be stored on D3, if there are more than 200 blocks available (check number of tracks available in SHOSZ). If not, D2 and L2 will be checked for availability. If all CRN are full, or there are no files available on the CRN (last column in SHOSZ), no analyses will run.

This sample will be stored in file >90243, the header will be A213990. The MS method is VOLP (created in DATAC years ago). The sample is in bottle 00 (Tekmar sampler on the "E" systems, -1 on the "A"), will be quantitated automatically and the data and quant output archived. The QUANT ID (target file of compounds to search for) is labeled ID624 and the Quant Output will be stored as ^90243 on CRN L2. The QT output file will not be automatically reported.

The GC parameters for the 5840 must be entered manually from the 5840 terminal.

```
Temp1 40
Time1  4
Rate   8
Temp2 220
Time2 10
FID SIG A
```

Make sure the packed column injection port is heated to 220.

The "SIG" must be entered after a power failure. The GC needs to think it has an internal detector.

LIST,LIST will print out existing conditions.

The inlet pressure on the 5840 instrument should be around 0.5 torr. If it isn't, make sure that the GC/MS valve is open.

The 5890 GC parameters are controlled by the method file (and each file is slightly different so make sure yours is documented). There are no valves to open on this instrument, the effluent from the column always goes through the jet separator into the mass spec. The normal jet separator pressure is 0.5 torr at oven temperature of 40 degrees.

Samples, blanks and standards can be run in DATAC or BAMON. When DATAC analyses are made during the day, the vessels can be cleaned and pre-purged during the bake step and used again immediately. Wait until the Tekmar is on DESORB READY before pressing the red button or typing "GO" to start the analysis on the "E" systems. The system can be set up in advance on the "A" system.

Short BAMON runs can also be made during the day, again removing the purge vessel during the desorb step, cleaning it and replacing it during the bake cycle to pre-purge it. Wait until the TEKMAR is on DESORB READY before typing "GO,#". If a "BAMON lock error" occurs (too many users on the system for BAMON to schedule its session), ask someone to log off, or shut down an ETUTL session (T2FIL, R2PRT) and try again.

SCREENING OF SOIL SAMPLES

All soils are screened by GC/FID before GC/MS analysis in order to determine the dilution factor needed. For medium to high samples, a portion of the sample extract is transferred to an automatic sample vial and injected on the GC/FID using the same run program as for RCRA Solvents. Approximate concentrations are calculated and the dilution factor determined.

Samples which have to be run as low levels are screened by the medium method preparation, if the samples smell badly, or previous samples from the site have had high concentration of analytes.

CONTAMINATION PROBLEMS

The most common contaminates are methylene chloride and acetone. These can enter the sample from the air or through a syringe that was used for other work. The surrogate solution, if contaminated, will "spike" each sample with these compounds. Therefore it is very important that the glassware and syringes used for this analysis be kept clean and away from any source of contamination (ie Prep Lab). If there is a high concentration of any compound in the blank, the source must be identified and eliminated.

Check for the presence of air (masses 40 and 44) in the mass spectrum of BFB daily. The abundance of either of these ions should be less than the abundance of mass 50 of BFB. Anything greater than that is an indicat of a problem and should be remedied before continuing with the analysi

MAINTENANCE

The GC/MS systems require very little daily maintenance, but it important to follow a few simple steps.

1. Change the septum every 20-30 injections. If the system is staying in tune, this could be once a month. If not, it could be once a week. A perforated septum will not seal well around the syringe needle and cause the BFB to blow back out of the column and result in low peak abundance. It is important that the GC oven be turned down to room temperature (30 degrees) or off on the 5890, and the flow to the column is turned off (wait a few minutes for back pressure to decrease) before removing the septum nut. Replace the septum and tighten the nut 1/4 turn past finger tight. Turn up the flow and allow the column to remain at room temperature for 10-15 minutes (heating the oven while there is air in the column will cause degradation of the column packing and shorten the life of the column).

2. The trap needs changing when the SPCC and/or CCC compounds no longer meet the criteria and recalibration is necessary. The traps generally last 1-2 months, depending on the type of samples analyzed.

3. Change the column when the response factors no longer meet the criteria and the GC peaks start to merge. The columns usually last 3-4 months of normal use. When changing a packed column, make sure to turn the carrier flow off and wait a few minutes for the back pressure to bleed off. The MSD pumps (rough and diffusion) need to be turned off and the source cooled. Closing the GC/MS valve on the 5840 isolates the oven so the column can be changed without taking the instrument down. Allow the new column to remain at room temperature for 30 minutes with helium flow before starting the conditioning cycle.

4. Flush the sample purge lines in the Tekmar with methanol if there is significant residual contamination (when baking out doesn't help) from a high concentration sample or one that bubbled over. Purging DI water (heated if possible) also aids in eliminating contamination.

5. Clean the source, quadrupole and/or change the multiplier when the response of BFB or any other compound decreases and none of the above measures help.

6. Update the mass axis calibration when the values for BFB ions in BFBCHK vary by more than ± 0.1 amu. This will help the QT program in identifying target compound quant ions.

SAFETY

The toxicity or carcinogenicity of chemicals used in these methods have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in these methods. The MSDS sheets which accompany the solutions are stored in the safety cabinet.

The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood (change the filters regularly).

Wear gloves when handling samples and dispose immediately. Consider all samples as potentially hazardous. Remember the hazard does not necessarily come from the analytes being tested for but from other substances in the matrix (i.e. PCB's, mercury, etc).

EPA Method 524.2 Drinking Water Report

SURROGATE LIST (spike conc)

Dichloroethane-d4.....	___	% Rec	(10)
Toluene-d8.....	___	% Rec	(10)
Bromofluorobenzene.....	___	% Rec	(10)

REGULATED CONTAMINANTS

	Conc	D.L.
Benzene.....	____	0.5
Carbon tetrachloride.....	____	0.5
1,4-Dichlorobenzene.....	____	0.2
1,2-Dichloroethane.....	____	0.5
1,1-Dichloroethene.....	____	0.5
1,1,1-Trichloroethane.....	____	0.5
Trichloroethene.....	____	0.2
Vinyl chloride.....	____	0.5
Bromobenzene.....	____	1.0
Bromodichloromethane.....	____	1.0
Bromoform.....	____	1.0
Bromomethane.....	____	1.0
Chlorobenzene.....	____	1.0
Chlorodibromomethane.....	____	1.0
Chloroethane.....	____	1.0
Chloroform.....	____	1.0
Chloromethane.....	____	1.0
o-Chlorotoluene.....	____	1.0
p-Chlorotoluene.....	____	1.0
Dibromomethane.....	____	1.0
1,3-Dichlorobenzene.....	____	1.0
1,2-Dichlorobenzene.....	____	1.0
1,2-Dichloroethene (trans).....	____	1.0
1,2-Dichloroethene (cis).....	____	1.0
Dichloromethane.....	____	1.0
1,1-Dichloroethane.....	____	1.0
1,1-Dichloropropene.....	____	1.0
1,2-Dichloropropane.....	____	1.0
1,3-Dichloropropane.....	____	1.0
1,3-Dichloropropene (cis).....	____	1.0
1,3-Dichloropropene (trans)....	____	1.0
2,2-Dichloropropane.....	____	1.0
Ethylbenzene.....	____	1.0
Styrene.....	____	1.0
1,1,2-Trichloroethane.....	____	1.0
1,1,1,2-Tetrachloroethane.....	____	1.0
1,1,2,2-Tetrachloroethane.....	____	1.0
Tetrachloroethene.....	____	1.0
1,2,3-Trichloropropane.....	____	1.0
Toluene.....	____	1.0
o-Xylene.....	____	1.0
m-,p-Xylene.....	____	1.0
Bromochloromethane.....	____	1.0
n-Butylbenzene.....	____	1.0
Dichlorodifluoromethane.....	____	1.0
Fluorotrichloromethane.....	____	1.0
Hexachlorobutadiene.....	____	1.0
Isopropylbenzene.....	____	1.0
p-Isopropyltoluene.....	____	1.0
Naphthalene.....	____	1.0
n-Propylbenzene.....	____	1.0
sec-Butylbenzene.....	____	1.0
tert-Butylbenzene.....	____	1.0
1,2,3-Trichlorobenzene.....	____	1.0
1,2,4-Trichlorobenzene.....	____	1.0
1,2,4-Trimethylbenzene.....	____	1.0
1,3,5-Trimethylbenzene.....	____	1.0

EMS # ____ ____

Analyst _____

GC/MS File _____

Date/Time _____

Multiplier 1.0
Units uG/L

Reviewed by _____

Date Reviewed _____

Pages (attached) ___

EMS LABORATORIES, INC., INDIANAPOLIS, INDIANA

EPA Method 624 (O502.3) EMS Sample # _____ Analyst_____

Reviewer_____ Review Date _____ Number of pages _____

GC/MS File _____ Date/Time of Analysis _____

C. Cal File : _____
Blank File : _____
MS/MSD File : _____

SURROGATE LIST

Dichloroethane-d4...	_____	% Rec
Toluene-d8.....	_____	% Rec
Bromofluorobenzene..	_____	% Rec

ANALYTE LIST		UNITS	
Acrolein.....	____	_____	50
Acrylonitrile.....	____	_____	70
Benzene.....	____	_____	5
Bromoform.....	____	_____	5
Carbon tetrachloride.....	____	_____	5
Chlorobenzene.....	____	_____	5
Chloroethane.....	____	_____	10
2-Chloroethylvinylether.....	____	_____	10
Chloroform.....	____	_____	5
Dibromochloromethane.....	____	_____	5
Bromodichloromethane.....	____	_____	5
1,1-Dichloroethane.....	____	_____	5
1,2-Dichloroethane.....	____	_____	5
1,1-Dichloroethene.....	____	_____	5
1,2-Dichloropropane.....	____	_____	5
trans-1,3-Dichloropropene.....	____	_____	5
Ethylbenzene.....	____	_____	5
Bromomethane.....	____	_____	10
Chloromethane.....	____	_____	10
Methylene chloride.....	____	_____	5
1,1,2,2-Tetrachloroethane.....	____	_____	5
Tetrachloroethene.....	____	_____	5
Toluene.....	____	_____	5
trans-1,2-Dichloroethene.....	____	_____	5
1,1,1-Trichloroethane.....	____	_____	5
1,1,2-Trichloroethane.....	____	_____	5
Trichloroethene.....	____	_____	5
Trichlorofluoromethane.....	____	_____	5
Vinyl chloride.....	____	_____	10

Dilution Factor _____ Detection Limit Multiplier _____

Also Detected Compounds Attached? (Y/N) _____

EMS LABORATORIES, INC., INDIANAPOLIS, INDIANA

SW846-8240 0510.3/0510.9 EMS Sample # _____ Analyst _____

Reviewer_____ Review Date _____ Number of pages _____

GC/MS File _____ Date/Time of Analysis _____

C. Cal File : _____
Blank File : _____
MS/MSD File : _____

SURROGATE LIST

Dichloroethane-d4...	_____	% Rec
Toluene-d8.....	_____	% Rec
Bromofluorobenzene..	_____	% Rec

ANALYTE LIST		UNITS	
Acetone.....	_____	_____	20
Acrolein.....	_____	_____	50
Acrylonitrile.....	_____	_____	70
Benzene.....	_____	_____	5
Bromodichloromethane.....	_____	_____	5
Bromoform.....	_____	_____	5
Bromomethane.....	_____	_____	10
Carbon disulfide.....	_____	_____	5
Carbon tetrachloride.....	_____	_____	5
Chlorobenzene.....	_____	_____	5
Chloroethane.....	_____	_____	10
Chloroform.....	_____	_____	5
Chloromethane.....	_____	_____	10
Dibromochloromethane.....	_____	_____	5
cis-1,3-Dichloropropene.....	_____	_____	5
Dichlorodifluoromethane.....	_____	_____	5
1,1-Dichloroethane.....	_____	_____	5
1,2-Dichloroethane.....	_____	_____	5
1,1-Dichloroethene.....	_____	_____	5
1,2-Dichloropropane.....	_____	_____	5
Ethylbenzene.....	_____	_____	5
Fluorotrichloromethane.....	_____	_____	5
2-Hexanone.....	_____	_____	10
Methylene chloride.....	_____	_____	5
Methyl ethyl ketone.....	_____	_____	10
4-Methyl-2-pentanone.....	_____	_____	10
Styrene.....	_____	_____	5
1,1,2,2-Tetrachloroethane.....	_____	_____	5
Tetrachloroethene.....	_____	_____	5
Tetrahydrofuran.....	_____	_____	25
Toluene.....	_____	_____	5
1,2-Dichloroethene (total).....	_____	_____	5
trans-1,3-Dichloropropene.....	_____	_____	5
1,1,1-Trichloroethane.....	_____	_____	5
1,1,2-Trichloroethane.....	_____	_____	5
Trichloroethene.....	_____	_____	5
Vinyl acetate.....	_____	_____	10
Vinyl chloride.....	_____	_____	10
Xylenes (total).....	_____	_____	5
Methyl-t-butyl ether.....	_____	_____	(10)

Dilution Factor _____ Detection Limit Multiplier _____

Also Detected Compounds Attached? (Y/N) _____

GC/MS Volatile methods

QAQC TYPE	CWA(524.2)	EPA(624)	RCRA(SW846) 3rd ed.
Initial Cal	%RSD ≤20 % ,re-cal "bad" compounds or use a cal curve.	%RSD ≤35% or cal curve	%RSD ≤30% (CCC's) rf meet SPCC criteria
Continuing Cal	BFB and cal check every 8 hours rf %D ≤ 30% 10 uG/L standard. ISTD areas must be >30% and <150% from initial cal	BFB Tune check. No time limit. Compare 20 uG/L standard with "Q" value range. Can re-cal single compounds. Use initial cal for sample conc.	BFB Tune check 12 hours 50 uG/L (12 hours). rf %D ≤ 25% (CCC's) rf meet SPCC criteria. Use daily calibration for sample conc.
Reagent Water Blank	Daily, no target compounds > detection limit	same	same (common solvents can be 5 X d.l.)
Reagent Water Spike	% Recovery 5 uG/L Daily, can replace reagent blank	% Recovery. 20 uG/L as needed if matrix spikes fail.	same. 50 uG/L at least weekly.
Low Level Water Spike	weekly 2 uG/L	*	*
Matrix Spike	not required	% Recovery Spike 5% of samples compare with "P". Spike with all compounds (20 uG/L).	% Recovery Spike 5% of samples compare with method recovery. Spike with CLP compounds.
Duplicate/Matrix Spike duplicate	Duplicate blank spikes quarterly.	Duplicate as required to assess precision.	% Recovery and RPD Spike 5% of samples compare with method recovery.
Surrogates	Required- 5 uG/L	Required (30 uG/L)	Specified in 8240- 50 uG/L
Internal Standards	Required- 5 uG/L	Required (30 uG/L)	Required- 50 uG/L

* not in method

ANALYTICAL STANDARD OPERATING PROCEDURES

AND ANALYST TRAINING

FOR ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS

BY GC/MS

THIS IS AN EXACT COPY OF
THE ORIGINAL DOCUMENT

DO NOT
DUPLICATE

DATE

EMS-HERITAGE, INDIANAPOLIS, INDIANA

9/90

MS-6

CONFIDENTIAL

SOP Correction FORM

Heritage Labs, Inc

SOP Number: MS-1

SOP Title: Analytical Standard Operating Procedures and Analyst Training for Analysis of Semi-Volatile Organic Compounds by GC/MS

Page #: 1, 2, 3, 5, 6, 7, 16, 18, 23, 24

Requested by : Anne Bradburn Date: 1/6/94

Correction: Delete all references to 8270, replace with 8270A
Delete all references to 3510, replace with 3510A

Reason (if applicable):

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager Signature: Gary A. Klingle Date: 1/6/94

100892

EMS Test Codes:

0501.3	EPA Method 625
0505.3	SW-846 8270 (RCRA)
0506.3	EPA Method 625 (Acid Only)
0507.3	EPA Method 625 (Base/Neutral Only)
0508.3	Appendix IX Semi-Volatile Organics, RCRA
0514.3	TCLP Semi-Volatile Organics, RCRA
0517.3	SW-846 8270 (Base Only)
0518.3	SW-846 8270 (Acid Only)
0523.3	TCLP Semi-Volatile Organics (Landban, CCWE)
0531.3	IDEM/RCRA Semi-Volatile Organics
	SDWA 525 (in process)
0901.1	CLP Semi-volatile Organics

ANALYTICAL STANDARD OPERATING PROCEDURES

Tuning and Calibration

Each system used for the analysis of volatile or semi-volatile compounds must be tuned to meet the abundance criteria listed below for DFTPP.

Mass	Target value 625/8270	525
51	30%-60%	10%-80%
68	< 2% of 69	< 2% of 69
70	< 2% of 69	< 2% of 69
127	40%-60%	10%-80%
197	< 1% of 198	< 2% of 198
198	100%	100% or > 50% of 442
199	5%-9%	5%-9% of 198
275	10%-30%	10%-60%
365	> 1%	> 1%
441	present and < 443	present and < 443
442	> 40% of 198	100% or > 50% of 442
443	17%-23% of 442	15%-24% of 442

These criteria can not (usually) be met on any of the instruments using the AUTOTUNE file (APEIO#). It is necessary to adjust the various lenses using MSCAL-Manual Tune. Run PARM RAMP and use the graphics cursor to modify the setpoint. The ratios of 69/219/502 should be around 100%/40%/2% for the MS's and 100%/25%-30%/2% on the MSD's. Run mass axis and width calibration and look at a profile scan before storing the tune and exiting the program.

The mass spectrometers are considered to be in tuning compliance for 12 hours after the injection (and passing the criteria) of the tuning compound. Any analytical run which lasts longer than 12 hours from the injection of DFTPP, must include a tune check at or before the 12 hours expire. Background correction may only be used to eliminate column bleed or instrument background ions. A hardcopy report of each tune check

(spectrum and mass listing) is kept in the run folder. Background correction technique will be recorded in the logbook.

The GC/MS systems must be initially calibrated at a minimum of 5 concentrations to determine the linearity of response. Method 625 and 8240 standards are run at 20, 50, 80, 120 and 160 uG/mL. Benzoic acid, 2,4-dinitrophenol, 2,4,5-trichlorophenol, the nitro-anilines, 4-nitrophenol, 2,4-dinitro-o-cresol and pentachlorophenol only require a 4 point calibration since detection at less than 50 uG/mL is difficult. Method 525 standards are analyzed at 0.1, 0.5, 1.0, 2.0, 5.0 and 10 uG/mL. Surrogates are calibrated in the same manner as target compounds.

Analyte-mixtures (toxaphene, chlordane and PCB's) and other compounds which are listed on the RCRA lists (semi-volatile) will be analyzed periodically. The PCB/pests will be run at the detection limit, the other compounds will be analyzed at ~10 times the detection limit, and the ID file updated with the retention time and response factor. Any sample which contains PCB/Pests will be sent to the GC/ECD group for quantitation (if it wasn't already assigned). The sample report will contain the note "PCB ---/(Pesticide) confirmed by GC/MS. If one or more of the RCRA compounds not in the daily standard are identified in a sample, a standard containing the compounds and the sample will be re-analyzed in the same run.

The internal standards and surrogates in use are;

625/8270

INTERNAL STANDARDS	SURROGATES
d4-1,4-Dichlorobenzene	2-Fluorophenol
d8-Naphthalene	d6-Phenol
d10-Acenaphthene	d5-Nitrobenzene
d10-Phenanthrene	2-Fluorobiphenyl
d12-Chrysene	2,4,6-Tribromophenol
d12-Perylene	d14-Terphenyl

525

INTERNAL STANDARDS/SURROGATES
These compounds are added to the sample before extraction.

d10-Acenaphthene
d10-Phenanthrene
d12-Chrysene
d12-Perylene

d14-Terphenyl can be added to the extract before analysis.

Relative response factors are calculated as follows:

$$RRF = \frac{\text{area (compound)}}{\text{area (ISTD)}} \times \frac{\text{concentration (ISTD)}}{\text{concentration (compound)}}$$

The percent standard deviation (% RSD) of the RRF's for each compound are also calculated and reported in the final calibration report (computer generated CBRPT). Each method has initial calibration requirements; for 525, %RSD must be less than 20% or a calibration curve must be used, for 625, %RSD must be less that 35% or a calibration curve must be used, and for 8270, the % RSD of a the "CCC" compounds must be less than 30% and the response factors of the "SPCC" compounds must be greater than 0.05.

Every sample will be spiked with the appropriate surrogate compounds. The compounds and recovery limits (determined by the average of thirty or more analyses and updated regularly) are:

	Spike amt (ug)	8270 WATER RECOVERY	8270 SOIL RECOVERY
2-Fluorophenol	200	21-100	25-121
d6-Phenol	200	10-91	24-113
d5-Nitrobenzene	100	35-114	23-120
2-Fluorobiphenyl	100	43-116	30-115
2,4,6-Tribromophenol	200	10-123	19-122
d14-Terphenyl	100	33-141	18-137

	625 WATER	TCLP*
2-Fluorophenol	6-98	25-74
d6-Phenol	10-62	17-55
d5-Nitrobenzene	43-135	37-117
2-Fluorobiphenyl	52-140	65-103
2,4,6-Tribromophenol	23-147	47-125
d14-Terphenyl	59-147	73-123

	525
d10-Acenaphthene	
d10-Phenanthrene	
d12-Chrysene	
d12-Perylene	

* only 1 standard deviation used (advisory only).

The semi-volatile surrogate is added to 1 liter (or original weight/volume) of sample before extraction.

If more than one surrogate per fraction is outside the accepted range without obvious matrix interference, the sample will be re-analyzed. Both analyses will be reported, for clients who will pay, if the problem persists. All other clients' reports will contain the note "Sample re-analyzed with no improvement in surrogate recovery".

A DI spike and matrix spike and matrix spike duplicate will be performed as directed in the method. The compounds used and the limits are discussed in the individual methods. The recovery of the spike compounds are determined by the formula:

$$\% \text{ Recovery} = \frac{(\text{Conc in spiked sample} - \text{conc in sample})}{\text{Spike concentration}} \times 100\%$$

The relative % difference (% RPD) is calculated for recoveries of each compound in the spike and spike duplicate. The formula is:

$$RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-recovery in spike D2-recovery in spike duplicate

BLANK ANALYSES

A method blank will be extracted once per twenty samples from the same submitter, (or with a group of >5 IDEM samples) or at least once per extraction page. The concentration of target compounds must be less than the detection limit except for the phthalate esters which can be 5 times the detection limit. A blank will be analyzed on each instrument, and the MS File name entered on the page attached to the prep sheet, AFTER THE BLANK PASSES (IS ACCEPTED). It will be easier if samples from a prep sheet are run on one instrument, so that the blanks don't have to be analyzed twice.

Any target compound present in the blank, above the detection level will be reported. Any sample containing a similar amount of the compound (outside the acceptable range) will be reported and the results flagge The sample will be re-extracted, when possible, when the source of the contamination is identified and removed.

IDEM requires that an instrument blank (vial of methylene chloride) be analyzed in each sequence containing their samples IF and ONLY IF a method blank is not included in that sequence.

SEMI-VOLATILE ANALYSIS BY GC/MS

ANALYSIS SUMMARY- Samples are extracted according to their matrix and regulation. Almost any matrix can be extracted for semi-volatile analysis.

Water- Method 525-Drinking waters are extracted by using a liquid-solid (SPE) extraction. Internal standards act as surrogates and are added before the extraction in this method only.

Method 625-Waters are extracted using liquid-liquid extraction or continuous extraction at various pHs.

SW846-3510 is a liquid-liquid extraction for 8270 and SW846-3520 uses continuous extraction for aqueous samples which form emulsions. Both call for pH adjustment during extraction.

Soil- Method 625 was established for waters only but other sample matrices submitted for this analyte list can be extracted, at the discretion of the analyst.

SW846-3540 is a soxhlet extraction and 3550 a sonication extraction for soils.

Oil- Only SW846-3580 addresses the extraction of oily/sludgy matrices.

The sample components are separated by injecting an aliquot of the concentrated methylene chloride extract into a high resolution fused silica capillary column and raising the temperature slowly. The effluent from the column dumps directly into the mass spec source. The mass spec scans for ions with masses between 33-500 amu for most methods, 525 requires that 45-450 amu be scanned. Identification is made by comparing the mass spectra and retention times of sample peaks to reference spectra and retention times in a data base. Reference spectra are obtained from analysis of calibration standards under the same conditions used for analysis. Quantitation is performed using the internal standard method, comparing the response of the quantitation ion of the compound to the ion of the compound used as the internal standard. Surrogates are added to all analyses.

Method 525 is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, raw source water or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} solid phase extraction cartridge. The analytes compatible with this extraction include the PNA's, pesticides, phthalates, and PCB's. (This method will be developed in 11/90)

Method 625 is used to determine the concentration of semi-volatile organic compounds present in methylene chloride extracts from municipal and industrial discharges (NPDES permits). The report for 0501.3 lists

the compounds on the NPDES permit in that order.

Method 8270 is used to analyze compounds in extracts of all types of solid waste matrices, soils and waters. The report for 0505.3 contains the 625 compounds along with compounds on the Hazardous Substance List, in alphabetical order. Additional compounds identified in the samples are reported. This is not the complete list of compounds with the potential of being analyzed by this method. Clients often request additional analytes which require calibration, when possible.

The method detection limit for 625 and 8270 compounds is 10 uG/L (1 mG/kG in low/medium soils) for most compounds in water, other compounds are reported at 25 uG/L (2.5 mG/kG in soils) and 50 uG/L (5.0 mG/kG). The method detection limits for 525 have not been verified by the lab, but run less than 0.1 uG/L for most analytes. All detection limits are corrected for sample dilution or variance from the method in the prep. The analyte lists with detection limits are included in Appendix I (report cover sheet).

The holding time for water samples is 7 days from date of collection to extraction and 14 days from date of collection to extraction for soils. Extracts must be analyzed within 40 days from the date of analysis for 625 and 8270. Method 525 samples must be analyzed within 30 days of extraction. CLP water samples must be extracted within 5 days from date of delivery and the soils within 10 and analyzed within 40 days.

QC SUMMARY

All methods require an initial demonstration of laboratory accuracy and precision. Analyze five to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration from 1 to 5 times the detection level. Calculate the measured concentration of each analyte, the mean concentration and mean accuracy (mean percentage of true value) and the precision (RSD) of the measurements. This is used to determine the MDL for the method and is also used as a training procedure to assure that the analyst can meet the precision and accuracy requirements of the analysis. All analysts must meet these criteria before starting a (new) analysis.

The system must meet DFTPP and continuing calibration check criteria before analysis of samples can begin.

After the DFTPP has met the target criteria, continuing calibration check standard is analyzed. ALL method calibration criteria must be met or the samples will be re-analyzed.

Some clients require that a method or instrument blank be analyzed in each sequence containing their samples.

STANDARD PREPARATION

STORE ALL STANDARDS AND SURROGATE SOLUTIONS IN THE FREEZER. ENTER ALL STANDARDS AND RECORD THE NUMBER OF THE INDIVIDUAL MIXES IN THE LOG BOOK AND THE LOT # WHEN A NEW VIAL IS OPENED. All pertinent information regarding the dilution of standards must be entered into the log book, in detail at least once (in the front of the logbook), and referred to each time a standard is made. Include the type of standard (525, 625, 8270, STD, ISTD, Surr), new standard number, analyst initials and date, and dilution instructions.

Standards for Method 525 are available from ULTRA at a concentration of 100 uG/mL. These will be diluted to a stock solution of 20 uG/mL (1:5 dilution of each to 1 mL of methanol).

Standards for calibrating 625 and 8270 are purchased from Supelco or Restek. All the CLP compounds are present in 9 Supelco "SUPELPREME" solutions. Add 80 uL of each of the 2000 uG/mL "SUPELPREME" (and 160 uL of the Base Surrogates (1000 uG/mL)) and 200 uL methylene chloride (final concentration 160 mL). The concentration of all the Restek standards is 2000 uG/L, but benzidine has been dropped so use the Supelco benzidines standard with the other 7 Restek standards.

Dilute the Supelco (or Restek) internal standard solution (4000 uG/mL) 1:10 in methylene chloride-make sure that all the compounds are in solution (warm to room temperature and shake to dissolve all precipitate) before dilution (final concentration 400 uG/mL).

Initial calibration

Method 525 will be calibrated at 0.1, 0.5, 1.0, 2.0, 5.0 and 10 uG/mL (as per the method). 5, 25, 50, 100, 250 and 500 uL of the 20 uG/mL stock will be diluted to 1 mL in methylene chloride. The concentration of internal standard and surrogate is 5 uG/mL in each standard. (Pentachlorophenol and toxaphene, if required, are calibrated at higher concentrations; penta at 4 times the other analytes and toxaphene at 10, 25, 50, 100, 200 and 250 uG/mL).

Methods 625 and 8270 are calibrated at 20, 50, 80, 120 and 160 uG/mL. The initial calibration solutions are made by diluting 12.5, 31, 50 and 75 uL of the 160 uG/mL stock in methylene chloride to 0.1 mL in a conical vial (100 uL of the 160 are taken for the 160 standard!). Ten uL of (400 uG/mL) ISTD solution is added to each vial.

Daily calibration checks

A 2.0 uG/mL standard will be used as the continuing calibration check for method 525.

The 625/8270 continuing calibration standard is made by adding 31 uL of the 160 stock with 69 uL of methylene chloride and adding 10 uL of the ISTD in a "cone" vial (final concentration 50 uG/L). The method criteria

will be discussed later.

STANDARD OPERATING PROCEDURES FOR INSTRUMENT LOGBOOKS

The instrument identification must be labeled on the front and include the dates covered. The inside cover must contain the names of the BAMON, TUNE, METHOD, IDFILE, CAL FILE, the name and initials of the analyst and group leader. The GC conditions for tune check and analysis, including the column used and temperature programming need to be listed also. The initials of the "logbook police" must also be listed at the top of a page for logbook review dates, errors identified, etc. (These may be added to the back of logbooks presently in use.) Logbooks should be reviewed regularly.

Sample runs must be entered into the instrument log book. Include sample (Tekmar) position, EMS #, dilution factor (if any), file name and time samples removed from the storage area. Also refer to the GC METHOD and BEDIT files used. All log book entries must be initialled and dated at the bottom of the list, the analyst initials must be labeled "analyst". All instrument maintenance should be entered in this book.

Method 525

The initial demonstration of laboratory accuracy must be performed before samples can be analyzed. The method validation requires that four to seven standards (at 2-5 uG/L) be analyzed and the mean and standard deviation calculated. The mean accuracy should be 70%-130% as calculated by

$$\frac{\text{average recovery}}{\text{spike concentration}} \times 100\%$$

and the RSD should be less than 30%. Some analytes, particularly the polycyclic hydrocarbons with molecular weights >250, are measured at concentrations below 2 uG/L, with a mean accuracy of 45-130% of true value.

The method detection limit is calculated by multiplying the standard deviation of each analyte result by 3.1427. The method detection limits must be sufficient to detect analytes at the required levels. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte.

Before any samples are analyzed, or any time a new supply of cartridges is received from a supplier, it must be demonstrated that a lab reagent blank is reasonably free of contamination (phthalate esters and silicon compounds). In the same experiment, it must be demonstrated that the particle size and packing of the SPE cartridge are acceptable. Consistent flow rate is an indication of acceptable particle size distribution and packing. One liter of water should pass through the cartridge in about 2 hours with a partial vacuum of about 13 cm (5 in.) of mercury.

Initial calibration- The DFTPP tune criteria (5 nG on column) must be met before calibration can take place. Method 525 will be calibrated at 0.1, 0.5, 1.0, 2.0, 5.0 and 10 uG/mL (as per the method). The concentration of internal standard and surrogate is 5 uG/mL in each standard. A 1 uL injection is required. (Pentachlorophenol and toxaphene, if required, are calibrated at higher concentrations; penta at 4 times the other analytes and toxaphene at 10, 25, 50, 100, 200 and 250 uG/mL). A medium level standard is analyzed and checked for:

1. GC performance- Anthracene and phenanthrene should be separated by baseline. Benz(a)anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley is greater than 25%, the GC column requires maintenance.

2. MS sensitivity- The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer that 99% of the compounds are recognized, system/software maintenance is required.

3. Lack of degradation of endrin (if a target compound). Examine a plot of the abundance of m/z 67 in the region of 1.05-1.5 of the retention time of endrin. This is the region of elution of endrin aldehyde, a thermal isomerization product of endrin. Confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is < 10% of the abundance of m/z 67 produced by endrin. If not, system maintenance is required (lower the injection port temperature and/or clean and silanize the liner).

When all performance criteria are met, the rest of the calibration can be run. The %RSD of the response factors must be less than 30% or a calibration curve may be generated.

Control charts are suggested in the method to chart the performance of analyte and surrogate measurements as a function of time. Until the mainframe LIMS computer can/will do this, a folder containing copies of the recovery of spikes and surrogates will be maintained. Variations of this data as well as internal standard and surrogate area over time will be monitored and corrective action taken when required (if areas fall to <50% from the initial calibration).

Daily calibration check-The MS tune must be verified at the beginning of each 8 hour shift. A medium concentration standard is then analyzed under the same MS conditions. The areas of internal standards and surrogates in continuing calibration checks should not be less than 30 % or greater than 50% from the most recent continuing calibration.

The response factors must be within 30% of the initial calibration as reported in CBCHK. If the calibration does not pass for a few compounds, but analysis is required for priority RUSH or holding times, at the discretion of the analyst and group leader, analysis can proceed with the analyte(s) in question flagged if present in samples and re-analyzed when the system is in control. Sample concentrations are calculated from the response factors of the daily calibration check.

Analyze samples. Set up the sequence so that the (estimated) injection time of the last sample is within 8 hours of the time the DFTPP passed.

Additional QC- Monitor the areas of the internal standard and surrogates in continuing calibration checks. (ACCORDING TO THE METHOD!!-In laboratory fortified blanks or samples, the areas of the internal standards and surrogates will not be constant because the volume of the extract will vary.) But the ratios of the areas should be reasonably constant in these samples. The addition of 10 uL of the recovery standard, terphenyl-d_{14} (500 uG/mL) to the extract is optional, and may be used to monitor the recovery of internal standards and surrogates in laboratory spiked blanks and samples. Internal standard recovery should be in excess of 70%.

A reagent blank must be extracted with each batch of samples and any time a new lot of cartridges or other reagents are received.

Extract a spiked blank with each batch of 20 samples or once each extraction page, sample permitting. The same recoveries as for the analysis verification must be met (and the results added to the control charts).

To prove that the sample matrix does not contain materials that interfere with method performance, analyze a sample spike for every 20 samples. Matrix independence should be established for every sample matrix analyzed regularly. Extract spike and spike duplicates regularly, to determine the precision and accuracy of the method and to prove the detection limits.

At least quarterly, replicates of laboratory fortified blanks (spiked and duplicate spike DI water) should be analyzed to determine the precision of the lab.

At least quarterly, analyze a quality control sample from an external source.

Method 625

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the initial startup as follows. The method validation step requires that four 100 uG/L standards be analyzed. The mean and standard deviation of the calculated results are calculated. These values must meet the method criteria as listed in TABLE 6 of the method. The procedure must be repeated for those analytes which fail these criteria.

The method detection limits are determined from the analysis of seven 10 uG/L standards, quantitated as usual (some phenols require extraction of 50 uG/L standards). The mean and standard deviation are calculated and the MDL determined by multiplying the standard deviation (of the seven analysis) by 3.1427.

Initial calibration- The DFTPP tune criteria (50 nG on column) must be met before calibration can take place. EPA Method 625 is calibrated at 20, 50, 80, 120 and 160 uG/L (although only three points are necessary). The ISTD concentration is 50 uG/L. The RSD for all compounds must be less than 35%.

Daily calibration-The MS tune must be verified at the start of each analytical sequence. A 50 uG/L standard is analyzed and the response factors must be within 20% of the initial calibration as reported in CBCHK. If these criteria are met, then the analysis continues. If th calibration does not pass for a few compounds, but analysis is required for priority RUSH or holding times, at the discretion of the analyst and group leader, analysis can proceed with the analyte(s) in question flagged if present in samples and re-analyzed when the system is in control. Alternatively, a new calibration (three point) curve can be prepared for that (those) compound(s). There is no time limit for the analysis of these samples, but sequences are kept to less than 24 hours. Sample quantitation is calculated using the response factor from the continuing calibration check standard.

Required QC-A minimum of 5% of the samples (per matrix) must be spiked with all analytes (at 100 uG/L), the results compared with %P in Method 625 Table 6 and reported. Spiked blanks should be analyzed once per 20 samples and the results compared to "P", but the frequency can be decreased if the sample spike recoveries regularly pass the criteria. The control limits for surrogates and spike recoveries are set from the analysis of 30 or more analyses as the mean $\pm$ 2 standard deviations for the warning limit and mean $\pm$ 3 standard deviations for the control limit. These values are updated quarterly.

METHOD 625 TABLE 6

	Limit for B (uG/L)	Range for X (uG/L)	Range for P (%)
2,4,6-Trichlorophenol	31.7	52.4-129.2	37-144
4-Chloro-3-methylphenol	37.2	40.8-127.9	22-147
2-Chlorophenol	26.7	36.2-120.4	23-134
2,4-Dichlorophenol	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	26.1	41.8-109.0	32-119
2-Nitrophenol	35.2	45.0-166.7	29-162
4-Nitrophenol	47.2	13.0-106.5	D-132
2,4-Dinitrophenol	49.8	D-172.9	D-191
4,6-Dinitro-2-methylphenol	93.2	53.0-100.0	D-181
Pentachlorophenol	48.9	38.1-151.8	14-176
Phenol	22.6	16.6-100.0	5-112
Acenaphthene	27.6	60.1-132.3	47-145
Benzidine			
1,2,4-Trichlorobenzene	26.1	57.3-129.2	44-142
Hexachlorobenzene	24.9	7.8-141.5	D-152
Hexachloroethane	24.5	55.2-100.0	40-113
Bis(2-chloroethyl)ether	55.0	42.9-126.0	12-158
2-Chloronaphthalene	13.0	64.5-113.5	60-118
1,2-Dichlorobenzene	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	71.4	8.2-212.5	D-262
2,4-Dinitrotoluene	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	29.6	68.1-136.7	50-158
Fluoranthene	32.8	42.9-121.3	26-137
4-Chlorophenylphenylether	33.4	38.4-144.7	25-158
4-Bromophenylphenylether	23.0	64.9-114.4	53-127
Bis(2-chloroisopropyl)ether	46.3	62.8-138.6	36-166
Bis(2-chloroethoxy)methane	34.5	49.2-164.7	33-184

METHOD 625 TABLE 6 (cont)

	Limit for s (uG/L)	Range for X (uG/L)	Range for P (%)
Hexachlorobutadiene	26.3	37.8-102.2	24-116
Hexachlorocyclopentadiene			
Isophorone	63.3	46.6-180.2	21-196
Naphthalene	30.1	35.6-119.6	21-133
Nitrobenzene	39.3	54.3-157.6	35-180
N-Nitroso-dimethylamine			
N-Nitroso-dipropylamine	55.4	13.6-197.9	D-230
N-Nitroso-diphenylamine			
bis(2-ethylhexyl)phthalate	41.1	28.9-136.8	8-158
Benzylbutylphthalate	23.4	D-139.9	D-152
Di-n-butylphthalate	16.7	8.4-111.0	1-118
Di-n-octylphthalate	31.4	18.6-131.8	4-146
Diethylphthalate	26.5	D-100.0	D-114
Dimethylphthalate	23.2	D-100.0	D-112
Benz(a)anthracene	27.6	41.8-133	33-143
Benzo(a)pyrene	39.0	31.7-148.0	17-163
Benzo(b)fluoranthene	38.8	42.0-140.4	24-158
Benzo(k)fluoranthene	32.3	25.2-145.7	11-162
Chrysene	48.3	44.1-139.9	17-168
Acenaphthylene	40.2	53.5-126	33-145
Anthracene	32.0	43.4-118.0	27-133
Benzo(g,h,i)perylene	58.9	D-195.0	D-219
Fluorene	20.7	71.6-108.4	59-121
Phenanthrene	20.8	65.2-108.7	54-120
Dibenz(a,h)anthracene	70.0	D-199.7	D-227
Indeno(1,2,3-cd)pyrene	44.6	D-150.9	D-171
Pyrene	25.2	69.6-100.0	52-115
Aldrin	39.0	7.2-152.2	D-166
Dieldrin	30.7	44.3-119.3	29-136

METHOD 625 TABLE 6 (cont)

	Limit for s (uG/L)	Range for X (uG/L)	Range for P (%)
Chlordane			
4,4'-DDD	31.0	D-134.5	D-145
4,4'-DDE	32.0	19.2-119.7	4-136
4,4'-DDT	61.6	D-170.6	D-203
α-Endosulfan			
β-Endosulfan			
Endosulfan sulfate	16.7	D-103.5	D-107
Endrin			
Endrin aldehyde	32.5	D-188.8	D-209
Heptachlor	37.2	D-172.2	D-192
Heptachlor epoxide	54.7	70.9-109.4	26-156
α-BHC			
β-BHC	31.5	41.5-130.6	24-149
δ-BHC	21.6	D-100.0	D-110
γ-BHC (Lindane)			
PCB 1260	54.2	19.3-121.0	D-164
Toxaphene			

Method SW846-8270

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the initial startup as follows. The method validation step requires that four 100 uG/L standards be analyzed. The mean and standard deviation of the calculated results are calculated. These values must meet the method criteria as listed in TABLE 6 of the EPA 625 method. The procedure must be repeated for those analytes which fail these criteria.

The method detection limits are determined from the analysis of seven 10 uG/L standards, quantitated as usual (some phenols require extraction of 50 uG/L standards). The mean and standard deviation are calculated and the MDL determined by multiplying the standard deviation (of the seven analysis) by 3.1427.

Initial calibration- The DFTPP tune criteria (50 nG on column) must be met before calibration can take place. Method 8270 is calibrated at 20, 50, 80, 120 and 160 uG/L. The ISTD concentration is 50 uG/L. The RSD must be less than 30% for those compounds identified as Calibration Check Compounds (CCC's). In addition the response factors must be greater than 0.05 for the compounds designated as System Performance Check Compounds (SPCC's).

SV CCC's	SV SPCC's
Acenaphthene	N-nitroso-di-n-propylamine
1,4-Dichlorobenzene	Hexachlorocyclopentadiene
Hexachlorobutadiene	2,4-Dinitrophenol
N-nitroso-di-n-phenylamine	4-Nitrophenol
Di-n-octylphthalate	
Fluoranthene	
Benzo(a)pyrene	
4-Chloro-3-methylphenol	
2,4-Dichlorophenol	
2-Nitrophenol	
Phenol	
Pentachlorophenol	
2,4,6-Trichlorophenol	

Only after the SPCC and CCC criteria are met are the systems ready for sample analysis.

A calibration standard containing as many of the target compounds as possible must be analyzed every twelve hours during an analytical run. The SPCC compounds must meet the same criteria as the initial calibration, the CCC compounds must be within ± 25% RSD for sample analysis to continue. While there are no criteria on the rest of the compounds, be alert that all compounds (especially phenols) have an area high enough to maintain the detection limit. The retention time for any internal standard can not change by more than 30 seconds, or the area of the internal standard by more than a factor of 2 (-50% to +100%) from the last calibration check. System maintenance and/or recalibra

is done if any of these criteria are not met. The only exception is if there are samples requiring immediate analysis (RUSH or holding time expired) and no other instrument is available. The sample results will be flagged accordingly. The system will be brought into compliance as soon as sample load permits. The response factors from this continuing calibration check analysis are used to calculate target compound concentrations in the entire run for SW846 methods (or until another calibration check standard is analyzed).

Analyze samples. Set up the sequence so that the (estimated) injection time of the last sample is within 12 hours of the time the DFTPP passed.

Required QC-A minimum of 5% of the samples (per matrix) must be spiked and duplicate spiked with the CLP analytes (at 50 uG/L for water and 50 uG/kG) and the % recoveries and RPD values compared with those in CLP. Spiked blanks should be analyzed once per 20 samples and the results compared to the same criteria, but the frequency can be decreased if the sample spike recoveries pass the criteria. Recovery criteria are being developed for TCLP samples, which are spiked with each target compounds on the basis of the original waste stream.

CLP MS/MSD Recovery Criteria

	SPIKE AMOUNT	WATER RECOVERY	WATER RPD	SOIL RECOVERY	SOIL RPD
Phenol	200 uG	12-89	42	26-90	35
2-Chlorophenol	200 uG	27-123	40	25-102	50
1,4-Dichlorobenzene	100 uG	36-97	40	28-104	27
N-nitroso-di-n-propylamine	100 uG	41-116	38	41-126	38
1,2,4-Trichlorobenzene	100 uG	39-98	28	38-107	23
4-Chloro-3-methylphenol	200 uG	23-97	42	26-103	33
Acenaphthene	100 uG	46-118	31	31-137	19
4-Nitrophenol	200 uG	10-80	50	11-114	50
2,4-Dinitrotoluene	100 uG	24-96	38	28-89	47
Pentachlorophenol	200 uG	9-103	50	17-109	47
Pyrene	100 uG	26-127	31	35-142	36

Extract Analysis

525-Add 10 uL of internal standard (terphenyl-d_{14}, 5 uG/L) to 100 uL of sample extract (final concentration 0.5 uG/mL). (Use a 25 uL syringe for the ISTD solution and a 500 uL syringe for the samples. Flush the syringe 5-10 times between samples.

625/8270-To prepare the extracts for analysis, add 10 uL of internal standard (400 uG/mL) solution to each 0.1 mL of extract. (Use a 25 uL syringe for the ISTD solution and a 500 uL syringe for the samples. Flush the syringe 5-10 times between samples.)

Samples must be entered into the log book. Include auto sampler position, EMS #, File number, BEDIT list name, temperature program (can be listed once and referred to) and time and date extracts were removed from the storage area. All log book entries must be dated and initialled.

Use BEDIT to update the sequence file with the correct sample description and FRN. Make a hard copy of the file (BLIST) to include in the run folder. Make sure that the files are consecutive and the Quant output file number matches the Data file number. Check that there are no duplicate file names and that the Quant file will be stored on the correct CRN (NOT AQ).

A typical printout will look like this:

```
Sequence File: BASVL2::L2

Tune File: KIMI01                          (Manual Tune File-MS#2)

CR List: B2,B3,B4                          (CRN to store the data)
CR Cut-off: 3000 blocks                    (Minimum amount of room on a disc
                                           required before starting an analysis)

                                            Report Data Archive
                                           Quant : : ID Archive
Number of samples:      15     Sample Size : : : : Output Archive
                                  Bottle : : : : : :
Samp Data File      Sample Name          : : : : : : :   Quant ID
 No. Method File    Misc Data            : : : : : : :   Quant Output
001) >9350B         A214665             01 2 Y M Y N Y   IDEPA4::B1
     SEMIV2                             Dil=1.000      ^9350B::B1
      REPRT OPTIONS: Label Meth:1, BG Sub, Scale time: 4.000
```

Etc.

The data from this analysis will be stored on B2, if there are more than 3000 blocks available (check number of tracks available in SHOSZ). If not, B3 and B4 will be checked for availability. If all CRN are full, no analysis will run.

This sample will be stored in file >9350B, the header will be A214665.

MS method is SEMIV2 (created in DATAC years ago). The sample is in auto sampler vial # 01, will be quantitated automatically and the data and quant output archived. The QUANT ID (target file of compounds to search for) is labeled AQSVL3 and the Quant Output will be stored as ^9350B on CRN B1. A medium report will be sent to REPRT terminal using chromatogram labeling "1", and background subtraction will be performed on all spectra reported. The chromatogram will be drawn out from 4 minutes to the end.

Sample Size is the auto sampler injection stroke. For the 7672 injector (on the 5987),

1 = Full stroke, 10 uL
2 = Presently set at 2 uL
3 = Presently set at 1 uL.

The 7673 injector is capable of injecting any amount of sample. Enter the injection volume directly.

If a "BAMON lock error" occurs (too many users on the system for BAMON to schedule its session), ask someone to log off, or shut down an ETUTL session (T2FIL, R2PRT) and try again.

CONTAMINANTS

There are few contaminants in the semi-volatile analysis. Almost all can be avoided at the prep stage by keeping the glassware scrupulously clean and by solvent rinsing glass wool, soxhlet thimbles and sodium sulfate. (Baking the sodium sulfate at 400 C in a muffle furnace before use is also necessary.) The compounds most likely to be present in the blanks are phthalates, hydrocarbons (C20-C30) and siloxane compounds. Only the presence of phthalates (which are on the target compound list) would be a reason to disallow an analytical run. The baseline of the chromatogram should be at least 1000 total counts. At this level, the compounds can be identified at the detection level but will not overrange the detector at the upper level. The abundance of air (masses 40 and 44) should be less that the abundance of mass 51 in the DFTPP spectrum, any more might suggest an air leak.

Daily maintenance of the 5880 GC and MS#2 includes:

1. Change the injector liner and septum every analysis run. Clean the injector seal (the metal liner at the bottom of the injection port, inside the large nut). Trim a short piece from the head of the analytical column daily, and more if tailing of phenols becomes evident.

2. Bake the source at 300-350C when the response of DFTPP and/or internal standards decreases. Clean the source if baking doesn't help.

3. Change the column when the retention time of DFTPP has shifted to the beginning of the analysis window, or the tailing of the phenols starts to adversely affect the integration (too much QAREA needed). Make sure to loosen the oven connection from the MS side so that the

connector can be used to withdraw the column. Measure the exa length of column needed to go into the source (mark it with white-out). Chip off the white-out after the column is installed (it might cause the column to crack).

4. Update the mass axis calibration when the values for DFTPP ions in TUNEDR vary by more than ± 0.1 amu. This will help the QT program in identifying target compound quant ions.

SAFETY

The toxicity or carcinogenicity of chemicals used in these methods have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in these methods. The MSDS sheets which accompany the solutions are stored in the safety cabinet.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc. Use the portable hood and change the filters regularly (annually).

Wear gloves when handling samples and dispose immediately. Consider all samples as potentially hazardous. Remember the hazard does not necessarily come from the analytes being tested for but from other substances in the matrix (i.e. PCB's, PNA's etc).

EMS LABORATORIES, INC., INDIANAPOLIS, INDIANA 46231

0501.3 EPA Method 625 Semi-volatiles ... EMS SAMPLE NUMBER _____

GC/MS File ..... _____ UNITS uG/KG
Date/Time of Analysis ..... _____ DL MULT _____
Continuing Calibration File .. _____ DILUTION _____

ANALYST _____ REVIEWER _____ DATE _____ # PAGES (ATTACHED) ____

SURROGATE LIST

2-Fluorophenol.....	_____	%	2-Fluorobiphenyl.....	____	%
Phenol-d5.....	_____	%	2,4,6-Tribromophenol.....	____	%
Nitrobenzene-d5.....	_____	%	Terphenyl-d14.....	____	%

ANALYTE LIST		D.L.			
2,4,6-Trichlorophenol.....	___	330	Di-n-octylphthalate.....	___	3
4-Chloro-3-methylphenol.....	___	330	Diethylphthalate.....	___	3
2-Chlorophenol.....	___	330	Dimethylphthalate.....	___	3
2,4-Dichlorophenol.....	___	330	Benz(a)anthracene.....	___	3
2,4-Dimethylphenol.....	___	330	Benzo(a)pyrene.....	___	3
2-Nitrophenol.....	___	330	Benzo(b)fluoranthene.....	___	3
4-Nitrophenol.....	___	1600	Benzo(k)fluoranthene.....	___	3
2,4-Dinitrophenol.....	___	1600	Chrysene.....	___	3
4,6-Dinitro-2-methylphenol..	___	1600	Acenaphthylene.....	___	3
Pentachlorophenol.....	___	1600	Anthracene.....	___	3
Phenol.....	___	330	Benzo(g,h,i)perylene.....	___	3
Acenaphthene.....	___	330	Fluorene.....	___	3
Benzidine.....	___	660	Phenanthrene.....	_	
1,2,4-Trichlorobenzene.....	___	330	Dibenz(a,h)anthracene.....	___	
Hexachlorobenzene.....	___	330	Indeno(1,2,3-cd)pyrene.....	___	
Hexachloroethane.....	___	330	Pyrene.....	___	
Bis(2-chloroethyl)ether.....	___	330	Aldrin.....	___	
2-Chloronaphthalene.....	___	330	Dieldrin.....	___	
1,2-Dichlorobenzene.....	___	330	Chlordane.....	___	16
1,3-Dichlorobenzene.....	___	330	p,p'-DDT.....	___	
1,4-Dichlorobenzene.....	___	330	p,p'-DDE.....	___	
3,3'-Dichlorobenzidine.....	___	660	p,p'-DDD.....	___	
2,4-Dinitrotoluene.....	___	330	alpha-Endosulfan.....	___	
2,6-Dinitrotoluene.....	___	330	beta-Endosulfan.....	___	
Fluoranthene.....	___	330	Endosulfan sulfate.....	___	
4-Chlorophenylphenylether...	___	330	Endrin.....	___	
4-Bromophenylphenylether....	___	330	Endrin aldehyde.....	___	
Bis(2-chloroisopropyl)ether.	___	330	Heptachlor.....	___	
Bis(2-chloroethoxy)methane..	___	330	Heptachlor epoxide.....	___	
Hexachlorobutadiene.....	___	330	alpha-BHC.....	___	
Hexachlorocyclopentadiene...	___	330	beta-BHC.....	___	
Isophorone.....	___	330	delta-BHC.....	___	
Naphthalene.....	___	330	gamma-BHC (Lindane).....	___	
Nitrobenzene.....	___	330	Arochlor-1016.....	___	1
N-Nitroso-dimethylamine.....	___	330	Arochlor-1221.....	___	1
N-Nitroso-dipropylamine.....	___	330	Arochlor-1232.....	___	1
N-Nitroso-diphenylamine.....	___	330	Arochlor-1242.....	___	1
Bis(2-ethylhexyl)phthalate..	___	330	Arochlor-1248.....	_	1
Benzylbutylphthalate.....	___	330	Arochlor-1254.....	___	
Di-n-butylphthalate.....	___	330	Arochlor-1260.....	___	1
			Toxaphene.....	___	1

EMS LABORATORIES, INC., INDIANAPOLIS, INDIANA 46231

0505.3 SW846-8270 Semi-volatiles ... EMS SAMPLE NUMBER _____

GC/MS File ..... _____ UNITS uG/L
Date/Time of Analysis ..... _____ DL MULT _____
Continuing Calibration File .. _____ DILUTION _____

ANALYST ____ REVIEWER _____ DATE _____ # PAGES (ATTACHED) ____

SURROGATE LIST

2-Fluorophenol.....	____	%	2-Fluorobiphenyl.....	____	%
Phenol-d5.....	____	%	2,4,6-Tribromophenol.....	____	%
Nitrobenzene-d5.....	____	%	Terphenyl-d14.....	____	%

TARGET COMPOUND LIST

		D.L.			
Acenaphthene.....	____	10	Isophorone.....	____	1
Acenaphthylene.....	____	10	2-Methylnaphthalene.....	____	10
Anthracene.....	____	10	Naphthalene.....	____	1
Benz(a)anthracene.....	____	10	2-Nitroaniline.....	____	5
Benzo(a)pyrene.....	____	10	3-Nitroaniline.....	____	5
Benzo(b)fluoranthene.....	____	10	4-Nitroaniline.....	____	5
Benzo(g,h,i)perylene.....	____	10	Nitrobenzene.....	____	1
Benzo(k)fluoranthene.....	____	10	N-Nitroso-diphenylamine.....	____	1
Benzyl Alcohol.....	____	10	N-Nitroso-di-n-propylamine..	____	1
Benzylbutylphthalate.....	____	10	Phenanthrene.....	____	1
Bis(2-chloroethoxy)methane..	____	10	2-Picoline.....	____	1
Bis(2-chloroethyl)ether.....	____	10	Pyrene.....	____	
Bis(2-chloroisopropyl)ether.	____	10	Pyridine.....	____	
Bis(2-ethylhexyl)phthalate..	____	10	Tetrachlorobenzenes.....	____	
4-Bromophenylphenylether....	____	10	Toluenediamine.....	____	
(9H-)Carbazole.....	____	10	1,2,4-Trichlorobenzene.....	____	
4-Chloroaniline.....	____	10	Benzoic Acid.....	____	5
2-Chloronaphthalene.....	____	10	4-Chloro-3-methylphenol.....	____	
4-Chlorophenylphenylether...	____	10	2-Chlorophenol.....	____	
Chrysene.....	____	10	2,4-Dichlorophenol.....	____	
Dibenz(a,h)anthracene.....	____	10	2,4-Dimethylphenol.....	____	
Dibenzofuran.....	____	10	4,6-Dinitro-2-methylphenol..	____	
1,2-Dichlorobenzene.....	____	10	2,4-Dinitrophenol.....	____	
1,3-Dichlorobenzene.....	____	10	2-Methylphenol.....	____	
1,4-Dichlorobenzene.....	____	10	4-Methylphenol.....	____	
3,3' -Dichlorobenzidine.....	____	20	2-Nitrophenol.....	____	
Diethylphthalate.....	____	10	4-Nitrophenol.....	____	
Dimethylphthalate.....	____	10	Pentachlorophenol.....	____	
Di-n-butylphthalate.....	____	10	Phenol.....	____	
Dinitrobenzenes.....	____	50	Tetrachlorophenol.....	____	
2,4-Dinitrotoluene.....	____	10	2,4,5-Trichlorophenol.....	____	
2,6-Dinitrotoluene.....	____	10	2,4,6-Trichlorophenol.....	____	
Di-n-octylphthalate.....	____	10			
Fluoranthene.....	____	10	Isopropylbiphenyls.....	____	
Fluorene.....	____	10	Chlorinated Dibenzofurans...	____	
Hexachlorobenzene.....	____	10			
Hexachlorobutadiene.....	____	10			
Hexachlorocyclopentadiene...	____	10			
Hexachloroethane.....	____	10			
Indeno(1,2,3-cd)pyrene.....	____	10			

GC/MS Semi-Volatile methods

QAQC TYPE	CWA(525)	EPA(625)	RCRA(SW846) 3rd ed.
Initial Cal	DFTPP Check (5 ng). 6 Stds (0.1-10 ng/uL) rf < 30%. Chromatographic separation of isomers. MDL's must meet regulatory limits.	DFTPP (50 ng/uL). %RSD <35% or cal curve.	DFTPP (50 ng/uL). %RSD <30% (CCC's) rf meet SPCC criteria.
Continuing Cal	DFTPP and Cal Check every 8 hours rf < 30%, ISTD areas >30%, <150% from initial cal.	DFTPP and Cal. check rf %D < 20% (no concentration specified) Can re-cal single compounds. Use daily calibration for sample concentration.	DFTPP and Cal. check 12 hours 50 uG/L (12 hours). rf %D < 25% (CCC's) rf meet SPCC criteria Use daily calibration for sample concentration.
Reagent Water Blank	Extract with each batch. Low background check required with each new batch of reagents.	Extract daily	same (phthalates can be 5 X d.l.)
Reagent Water Spike	Extract with each batch.	% Recovery. As needed if matrix spikes fail.	same. At least weekly.
Low Level Water Spike	*	*	*
Matrix Spike	% Recovery Spike 5% of samples (all types). Determine lab criteria. Spike at 2-5 uG/L.	% Recovery Spike 5% of samples compare with "P". Spike with all compounds. (100 uG/L).	% Recovery Spike 5% of samples compare with method recovery. Spike with CLP compounds.
Duplicate/Matrix Spike duplicate	Spike Duplicate 5% (all types).	Duplicate as required to assess precision.	% Recovery and RPD Spike 5% of samples compare with method recovery. Spike with CLP compounds.
Surrogates	ISTD compounds used as surrogates	Required	Specified in 8270
Internal Standards	see above.	Required	Required

* not found in method

Revision Date: October 9, 1990

PCB/PESTICIDE ANALYSIS BY GC ECD

EMS Test Codes: 0305.1 (PCB/Pesticide analyses) or 0164.1, 0164.2, 0164.3 and 0164.4 (Pesticide analyses)
Method Quote: SW846-8080 (RCRA)

Referenced Procedures
Methods: SW846-3510 and SW846-3550

I. Introduction:

These tests are used to analyze for solvent extractable Polychlorinated Biphenyls (PCB) and Pesticides in water and solid samples. The analysis is performed by capillary gas chromatography with an electron capture detector. The instruments being used presently are Hewlett-Packard GCs (Model 5880 and Model 5890) with J+W DB-608 megabore columns and J+W DB-5 capillary columns. All pesticide analyses must be run on two columns of different polarity since they are, normally, single peaked analytes. In most cases the DB-608 is used as the primary column for the quantitation of the analytes, and the DB-5 is used for confirmation.

A. Tests - 0305.1, 0164.1, 0164.2, 0164.3 and 0164.4 (for analyte list, see table on page 53)
B. Method detection limit - see table on page 53
C. Containers - All samples should be submitted in glass containers with teflon lined caps. Plastic containers should be avoided if at all possible. Waters should be submitted in a 1 liter amber glass bottle and should be completely filled. Solid samples should be submitted in a 250 mL wide mouth bottle and should contain at least 30 grams of sample. The methods require a matrix spike and matrix spike duplicate at a frequency of 10% of the samples, therefore extra sample should be included to accommodate this requirement.
D. Preservatives - none
E. Holding times
   Waters: 7 days from sampling (5 days from receipt)
   Solids: 14 days from sampling (12 days from receipt)
   NOTE: Samples should be submitted to the lab within 24 hours of sampling to assure extraction within holding time.
F. Extract holding time - 14 days

SOP Correction FORM
HERITAGE LABORATORIES, INC

SOP Number: OLD FORMAT

SOP Title: PCB / Pesticides Analysis by GC ECD

Page #: 1, 3

Requested by : Lisa Julian Date: 1-5-94

Correction: SW846-3510 ~~and SW846 3550~~ LAJ 1-5-94
changed to SW846-3510A

Reason (if applicable): Updated Method cited

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: Gary A. Klingle Date: 1/6/94
100892

PCB/Pesticide Analysis
Analyte List and Detection Limits

Analyte	Detection Limits mg/L waters	Detection Limits mg/Kg solids	Analytes tested for 0305.1	0164.X .1	0164.X .2	0164.X .3
alpha-BHC	0.00005	0.0080	X	X		
beta-BHC	0.00005	0.0080	X	X		
delta-BHC	0.00005	0.0080	X	X		
gamma-BHC	0.00005	0.0080	X	X	X	X
Heptachlor	0.00005	0.0080	X	X		X
Aldrin	0.00005	0.0080	X	X		
Hept.Epoxide	0.00005	0.0080	X	X		X
Endosulfan I	0.00005	0.0080	X	X		
Dieldrin	0.0001	0.016	X	X		
4,4'-DDE	0.0001	0.016	X	X		
Endrin	0.0001	0.016	X	X	X	X
Endosulfan II	0.0001	0.016	X	X		
4,4'-DDD	0.0001	0.016	X	X		
Endo.sulfate	0.0001	0.016	X	X		
4,4'-DDT	0.0001	0.016	X	X		
Methoxychlor	0.0005	0.080	X	X	X	X
Endrin ketone	0.0001	0.016	X	X		
a. Chlordane	0.0005	0.080	X	X		X
g. Chlordane	0.0005	0.080	X	X		X
Toxaphene	0.0010	0.080	X	X	X	X
Aroclor 1016	0.0005	0.160	X			
Aroclor 1221	0.0005	0.080	X			
Aroclor 1232	0.0005	0.080	X			
Aroclor 1242	0.0005	0.080	X			
Aroclor 1248	0.0005	0.080	X			
Aroclor 1254	0.0010	0.160	X			
Aroclor 1260	0.0010	0.160	X			
Tech. Chlor.	0.0010	0.160				X

NOTE: Detection limits are subject to change depending on the amount of sample available and the interferences in the sample.

NOTE: Test Code 0164.4 is used for odd analytes.

II. Extraction Procedures:

The type of extraction is dependent on the sample matrix and requirements of the client. There are two different extraction methods currently used for PCB/Pesticide analyses.

A. **Water Extraction - Prep Code: P233.1**
Reference Method: SW846-3510

1. Theory

The water samples are extracted using methylene chloride by a liquid/liquid extraction, with a subsequent solvent exchange into hexane for analysis by GC. Any PCB or pesticide analyte in the water sample will be more soluble in the methylene chloride and will be extracted from the water. Once extracted from the water any PCB or pesticide analyte is transferred to hexane by evaporation and concentration of the solvents. Once in hexane the extract is cleaned up using an alumina column, to remove as much of the interfering contaminants as possible.

2. Apparatus

1000 mL Graduated cylinder
100 mL Graduated cylinder
2000 mL Separatory funnel with teflon stopcock and stopper
Kuderna-Danish (KD) evaporative concentrator:
10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
Glass Moonie funnel - 20 mm
Glass wool
Hot water bath
10 mL volumetric flasks
Volumetric pipets - various sizes
Disposable pasteur pipets
Alumina columns
Boiling chips
Alkacid - pH test paper
Teflon stir rods (in case of emulsions)
Autosampler vials with crimp top caps
2 Dram vials with teflon lined lids

3. Reagents

Methylene chloride - optima grade
Hexane - optima grade
Acetone - certified ACS
Sodium sulfate - granular, anhydrous - baked at 400°C for 24 hours
Surrogate solution :
1.0 mg/L DBC and 1.0 mg/L 2,4,5,6-tetrachloro-m-xylene in methanol
10 N Sodium hydroxide (for adjusting pH)
1+1 Sulfuric acid (for adjusting pH)

4. Procedure

All glassware should be cleaned with hot soapy (microsoap) water, rinsed with tap water, distilled water and a final rinse with acetone. Immediately before use all glassware should be solvent rinsed three times with methylene chloride. The samples should be removed from the cooler and allowed to warm to ambient temperature before extracting. Check the pH of the sample using alkacid paper to assure it is between a pH of 5 and 9. Adjust the pH with 10 N sodium hydroxide or 1+1 sulfuric acid if necessary. When using the entire sample for analysis, mark the level of the sample in the bottle with liquid paper so the sample volume can be determined. If only a portion of the sample is to be analyzed, measure out the desired amount in a clean, methylene chloride rinsed graduated cylinder. Record the volume of sample analyzed on the prep bench sheet.

Quantitatively transfer the sample into a 2000 mL separatory funnel. If the sample volume used is less than 600 mL, a 1000 mL (or smaller) separatory funnel may be used. Place the funnel in a ring stand and add 1.0 mL of the pesticide surrogate solution to the sample. Rinse the sample bottle (or graduated cylinder) with 60 mL of methylene chloride and add the rinse to the separatory funnel. If the entire sample was used, fill the empty sample bottle to the liquid paper mark. Pour the water into a graduated cylinder and record the volume on the prep sheet. Vigorously shake the separatory funnel for two minutes, venting the funnel to release pressure as needed. Place the funnel back into the ring stand and allow the methylene chloride and water layers to separate for about 5 minutes. If an emulsion forms, the emulsion must be broken up before continuing. Refer to section 6, page 57 for procedures for breaking emulsions.

Assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask. Add two to three boiling chips to the KD flask. Plug a glass moonie funnel with a piece of glass wool and fill the funnel 3/4 full with baked granular sodium sulfate. Rinse the

sodium sulfate (in the funnel) three times with methylene chloride and allow to drain. Place the moonie funnel on top of the KD apparatus. Drain the methylene chloride (bottom) layer from the separatory funnel into the KD apparatus by passing through the sodium sulfate. The funnel with the sodium sulfate acts as a drying column to retain any water included with the methylene chloride. Repeat the extraction procedure two times by adding 60 mL of methylene chloride to the separatory funnel and extract in the same manner, again draining the methylene chloride layer into the KD apparatus.

Rinse the sodium sulfate funnel with approximately 50 mL of methylene chloride and allow the solvent to drain. Remove the funnel and place a solvent rinsed three ball macro-Snyder column on the KD apparatus. Concentrate the extracts by evaporating the solvent on a hot water bath. Place the tip of the concentrating ampule into a boiling water bath. Tap the KD apparatus gently until the solvent begins to boil and the balls begin to "chatter", then lower the KD until the boiling water is at about the level of the 10 mL mark on the concentrating ampule. Concentrate the extract until about 1 mL is left in the concentrating ampule. Remove the KD apparatus from the water bath and allow it to cool and drain. Remove the macro-Snyder column and add 50 mL of hexane to the KD flask. Replace the macro-Snyder column and pre-wet it with a few mL of hexane. Concentrate the extract to 1 mL on a hot water bath and remove. Rinse down the macro-Snyder column with a few mL of hexane then allow to drain and cool. Remove the macro-Snyder column and the KD flask from the ampule, rinsing the ground glass joints with hexane.

Attach a hexane rinsed two ball micro-Snyder column to the concentrating ampule and concentrate the sample to less than 1 mL in the hot water bath. During the final concentration the inside wall of the micro-snyder must be rinsed down several times. It is critical that the extract not be allowed to boil dry. Bring the volume of the extract up to exactly 1 mL in the concentrating ampule, with hexane.

<u>Alumina Clean up</u>

Prepare an alumina column by adding 3 grams of activity III alumina to a glass wool plugged disposable pipet. Place the alumina column in the top of a hexane rinsed 10 mL volumetric flask. Add 1 mL of acetone to the hexane extract in the concentrating ampule. Transfer the hexane/acetone extract to the alumina column and allow to drain into the 10 mL volumetric flask. Rinse the concentrating ampule three times with hexane (approximately 1 mL aliquots) and add each rinse to the alumina column. Finally, elute the alumina column with

about 5 mL of hexane. Bring the extract to a final volume of 10 mL in the volumetric flask. Transfer a 1 mL aliquot of the extract to an autosampler vial for analysis by GC. Transfer the remainder of the extract to a 2 dram vial for storage.

5. Quality control

A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 1000 mL of DI water in the same manner as the samples

A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 1000 mL of DI water with 1 mL of a pesticide standard mix. (For analytes and concentrations see section IV, D page 32.) The standard is then extracted in the same manner as the samples.

A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide at least 3 liters of one sample, in each group of ten. All three liters of the sample should be composited into a clean, methylene chloride rinsed solvent bottle. The sample should be extracted using 1000 mL and the rest of the sample should be divided between the SPI02 and DPS02. The spikes are prepared by spiking with 1 mL of the pesticide standard mix, and then extracting in the same manner as the sample.

6. Procedure for Breaking Emulsions

If the emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration, centrifugation, or other physical methods.

Emulsion Breakers

1. Use a solvent rinsed teflon stir bar, or a 9" disposable pipet, to stir the emulsion. This should break up most of the emulsion so that 75% of the solvent can be drained.

If stirring does not break the emulsion then any of the following methods could be tried.

2. Fill a funnel with solvent rinsed glass wool. Slowly drain the emulsion through the funnel into a flask. If the emulsion does not flow through easily, stir the contents and glass wool with a teflon stirring rod. Rinse the glass wool with methylene chloride and squeeze the excess out with the teflon rod. Carefully, pour the contents of the flask back into the separatory funnel and allow the layers to separate. Usually this separates the emulsion into the two layers. Drain the methylene chloride layer into the KD flask.

3. Drain the emulsion into a 250 mL beaker which contains approximately one inch of anhydrous sodium sulfate. Break up the sodium sulfate with a teflon stir rod, and carefully pour the contents of the beaker back into the separatory funnel. Allow the layers to separate and drain the methylene chloride layer into the KD apparatus. Rinse the sodium sulfate in the beaker with methylene chloride and pour the rinse into the flask.

4. If none of these methods will break the emulsion, drain the emulsion layer into a small (250 mL) separatory funnel and add about 2 mL of sulfuric acid to break the emulsion. Drain only the methylene chloride layer into the KD flask. Discard the water layer.

PCB/Pesticide Water Extraction - Lab bench copy

I. Apparatus
   A. 1000 mL Graduated cylinder
   B. 100 mL Graduated cylinder
   C. 2000 mL Separatory funnel with teflon stopcock and stopper
   D. Kuderna-Danish (KD) evaporative concentrator: 10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
   E. Glass Moonie funnel - 20 mm
   F. Glass wool
   G. Hot water bath
   H. 10 mL volumetric flasks
   I. Volumetric pipets - various sizes
   J. Disposable pasteur pipets
   K. Alumina columns
   L. Boiling chips
   M. Alkacid - pH test paper
   N. Teflon stir rods (in case of emulsions)
   O. Autosampler vials with crimp top caps
   P. 2 Dram vials with teflon lined lids

II. Reagents
   A. Methylene chloride - optima grade
   B. Hexane - optima grade
   C. Acetone - certified ACS
   D. Sodium sulfate - granular, anhydrous - baked at 400°C for 24 hours
   E. Surrogate solution: 1.0 mg/L DBC and 1.0 mg/L 2,4,5,6-tetrachloro-m-xylene in methanol
   F. 10 N Sodium hydroxide (for adjusting pH)
   G. 1+1 Sulfuric acid (for adjusting pH)

III. Procedure

   A. All glassware should be cleaned with hot soapy (microsoap) water, rinsed with tap water, distilled water and a final rinse with acetone.
   B. Immediately before use all glassware should be solvent rinsed three times with methylene chloride.
   C. The samples should be removed from the cooler and allowed to warm to ambient temperature before extracting.
   D. Check to pH of the sample using alkacid paper to assure it is between a pH of 5 and 9. Adjust the pH with 10 N sodium hydroxide or 1+1 sulfuric acid if necessary.

PCB/Pesticide Water Extraction - Lab bench copy
(continued)

E. When using the entire sample for analysis, mark the level of the sample in the bottle with liquid paper so the sample volume can be determined. If only a portion of the sample is to be analyzed, measure out the desired amount in a clean, methylene chloride rinsed graduated cylinder. Record the volume of sample analyzed on the prep bench sheet.

F. Quantitatively transfer the sample into a 2000 mL separatory funnel.
NOTE: If the sample volume used is less than 600 mL, a 1000 mL (or smaller) separatory funnel may be used.

G. Place the funnel in a ring stand and add 1.0 mL of the pesticide surrogate solution to the sample.

H. Rinse the sample bottle (or graduated cylinder) with 60 mL of methylene chloride and add the rinse to the separatory funnel.

I. If the entire sample was used, fill the empty sample bottle to the liquid paper mark. Pour the water into a graduated cylinder and record the volume on the prep sheet.

J. Vigorously shake the separatory funnel for two minutes, venting the funnel to release pressure as needed.

K. Place the funnel back into the ring stand and allow the methylene chloride and water layers to separate for about 5 minutes.

L. If an emulsion forms, the emulsion must be broken up before continuing. Refer to section on methods of breaking emulsions.

M. Assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask.

N. Add two to three boiling chips to the KD flask.

O. Plug a glass moonie funnel with a piece of glass wool and fill the funnel 3/4 full with baked granular sodium sulfate.

P. Rinse the sodium sulfate (in the funnel) three times with methylene chloride and allow to drain.

Q. Place the moonie funnel on top of the KD apparatus.

R. Drain the methylene chloride (bottom) layer from the separatory funnel into the KD apparatus by passing through the sodium sulfate.
NOTE: The funnel with the sodium sulfate acts as a drying column to retain any water included with the methylene chloride.

S. Repeat the extraction procedure two times by adding 60 mL of methylene chloride to the separatory funnel and extract in the same manner, again draining the methylene chloride layer into the KD apparatus.

PCB/Pesticide Water Extraction - Lab bench copy
(continued)

T. Rinse the sodium sulfate funnel with approximately 50 mL of methylene chloride and allow to drain completely.
U. Remove the funnel and place a solvent rinsed three ball macro-Snyder column on the KD apparatus.
V. Concentrate the extracts by evaporating the solvent on a hot water bath.
W. Place the tip of the concentrating ampule into a boiling water bath. Tap the KD apparatus gently until the solvent begins to boil and the balls begin to "chatter", then lower the KD until the boiling water is at about the level of the 10 mL mark on the concentrating ampule.
X. Concentrate the extract until about 1 mL is left in the concentrating ampule.
Y. Remove the KD apparatus from the water bath and allow it to cool and drain.
Z. Remove the macro-Snyder column and add 50 mL of hexane to the KD flask.
AA. Replace the macro-Snyder column and pre-wet it with a 2 to 3 mL of hexane.
BB. Concentrate the extract to 1 mL on a hot water bath and remove.
CC. Rinse down the macro-Snyder column with a few mL's of hexane then allow to drain and cool.
DD. Remove the macro-Snyder column and the KD flask from the ampule, rinsing the ground glass joints with hexane.
EE. Attach a hexane rinsed two ball micro-Snyder column to the concentrating ampule and concentrate the sample to less than 1 mL in the hot water bath.
FF. During the final concentration the inside wall of the micro-snyder must be rinsed down several times.
NOTE: It is critical that the extract not be allowed to boil dry.
GG. Bring the volume of the extract up to exactly 1 mL in the concentrating ampule, with hexane.

<u>Alumina Clean up</u>

HH. Prepare an alumina column by adding 3 grams of activity III alumina to a glass wool plugged disposable pipet.
II. Place the alumina column in the top of a hexane rinsed 10 mL volumetric flask.
JJ. Add 1 mL of acetone to the hexane extract in the concentrating ampule.
KK. Transfer the hexane/acetone extract to the alumina column and allow to drain into the 10 mL volumetric flask.
LL. Rinse the concentrating ampule three times with hexane (approximately 1 mL aliquots) and add each rinse to the alumina column.

PCB/Pesticide Water Extraction - Lab bench copy
(continued)

MM. Finally elute the alumina column with about 5 mL of hexane.
NN. Bring the extract to a final volume of 10 mL in the volumetric flask.
OO. Transfer a 1 mL aliquot of the extract to an autosampler vial for analysis by GC.
PP. Transfer the remainder of the extract to a 2 dram vial for storage.

IV. Quality control

A. A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 1000 mL of DI water in the same manner as the samples.
B. A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 1000 mL of DI water with 1 mL of a pesticide standard mix. (For analytes and concentrations see section IV, D page 32.) The standard is then extracted in the same manner as the samples.
C. A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide at least 3 liters of one sample, in each group of ten. All three liters of the sample should be composited into a clean, methylene chloride rinsed solvent bottle. The sample should be extracted using 1000 mL and the rest of the sample should be divided between the SPI02 and DPS02. The spikes are prepared by spiking with 1 mL of the pesticide standard mix, and then extracting in the same manner as the sample.

Procedure for Breaking Emulsions - Lab bench copy

If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration, centrifugation, or other physical methods.

Emulsion Breakers

I. Stirring
Use a solvent rinsed teflon stir bar, or a 9" disposable pipet, to stir the emulsion. This should break up most of the emulsion so that 75% of the solvent can be drained.

If stirring does not break the emulsion then any of the following methods could be tried.

II. Glass Wool
- A. Fill a funnel with solvent rinsed glass wool.
- B. Slowly drain the emulsion through the funnel into a flask. If the emulsion does not flow through easily, stir the contents and glass wool with a teflon stirring rod.
- C. Rinse the glass wool with methylene chloride and squeeze the excess out with the teflon rod.
- D. Carefully, pour the contents of the flask back into the separatory funnel and allow the layers to separate.
- E. Drain the methylene chloride layer into the KD flask.

III. Sodium sulfate
- A. Drain the emulsion into a 250 mL beaker which contains approximately one inch of anhydrous sodium sulfate.
- B. Break up the sodium sulfate with a teflon stir rod.
- C. Carefully pour the contents of the beaker back into the separatory funnel.
- D. Allow the layers to separate and drain the methylene chloride layer into the KD apparatus.
- E. Rinse the sodium sulfate in the beaker with methylene chloride and pour the rinse into the flask.

IV. Sulfuric acid
- A. If none of these methods will break the emulsion, drain the emulsion layer into a small 250 mL separatory funnel.
- B. Add about 2 mL of sulfuric acid to break the emulsion.
- C. Drain only the methylene chloride layer into the KD flask.
- D. Discard the water layer.

B. Solid (soil) Extraction - Prep code: P236.1 or P236.0
(for shared prep, with Semi-Vols)
Reference Method: SW846-3550

1. Theory

This procedure is used for extracting semivolatile and nonvolatile organic compounds from solids such as soils, sludges, and wastes. The nonvolatile PCB and pesticide analytes are solvent extractable. The use of a sonication process ensures intimate contact of the sample matrix with the extraction solvent. After extraction, the sample extract is cleaned up using Gel Permeation chromatography, and a solvent exchange into hexane is performed. The hexane extract is then cleaned up using an alumina column before analysis by GC.

2. Apparatus

Balance
400 mL beakers (thick walled)
100 mL graduated cylinder
Tekmar Ultrasonic Cell disrupter:
- Controller - 500 watt with pulsing capability,
- Disrupter horn - solid, 3/4 inch standard tip,
- Sound enclosure and lab jack

Kuderna-Danish (KD) evaporative concentrator:
- 10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column

Glass Moonie funnel - 20 mm
Glass wool
Hot water bath
10 mL volumetric flasks
Volumetric pipets - various sizes
Disposable pasteur pipets
Alumina columns
Boiling chips
Teflon stir rods
Autosampler vials with crimp top caps
Screw top autosampler vials with teflon liners and lids
2 Dram vials with teflon lined lids

3. Reagents
   Methylene chloride - optima grade
   Acetone - certified ACS
   (prepare a 1:1 methylene chloride/acetone mix)
   Hexane - optima grade
   Sodium sulfate - granular, anhydrous, baked at 400°C for 24hr
   Sodium sulfate - powdered, anhydrous, baked at 400°C for 24hr
   Surrogate solution:
   1.0 mg/L DBC and 1.0 mg/L 2,4,5,6-tetrachloro-m-xylene in methanol
   Alumnia (activity III)

4. Procedure

All glassware should be cleaned with hot soapy (microsoap) water, rinsed with tap water, distilled water and a final rinse with acetone. Immediately before use all glassware should be solvent rinsed three times with methylene chloride. The samples should be removed from the cooler and allowed to warm to ambient temperature before extracting. Decant and discard any water layer on a sediment sample. Mix the sample thoroughly. Discard any foreign objects such as sticks, leaves and rocks. Weigh approximately 30 grams of sample to the nearest 0.1 g into a 400 mL beaker. Add 60 grams of anhydrous, powdered sodium sulfate to the beaker and mix well. The sample should have a sandy texture at this point. Immediately add 100 mL of 1:1 methylene chloride/acetone to the sample.

NOTE: The pH of the sample and the percent moisture should be determined. These are performed in the General Inorganic Lab.

Rinse the disrupter horn three times with the methylene chloride/acetone mix, and then place the beaker onto the lab jack in the ultrasonic cell disrupter sound enclosure. Raise the lab jack to the point where the bottom surface of the tip of the horn is about 1/2 inch below the surface of the solvent but above the sediment layer. Sonicate for 3 minutes using the 3/4 inch horn with the output control knob set at 10 and the mode switch on "pulse" and % duty cycle knob set at 50%.

NOTE: If using a dual controller, be sure both horn are identical and that the horn tips are submersed before turning on.

Assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask. Add two to three boiling chips to the KD flask. Plug a glass moonie funnel with a piece of glass wool and fill the funnel 3/4 full with baked granular sodium sulfate. Rinse the sodium sulfate (in the funnel) three times with methylene

chloride and allow to drain. Place the moonie funnel on top of the KD apparatus. Decant and filter the extract through the sodium sulfate into the KD apparatus. The funnel with the sodium sulfate acts as a drying column to retain any water included with the methylene chloride. Repeat the extraction procedure two times with two additional 100 mL portions of 1:1 methylene chloride/ acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean teflon stir rod. Decant off the extract after each sonication. After the final sonication and filtration, rinse the sodium sulfate with 1:1 methylene chloride/ acetone and add the rinse to the KD apparatus, through the sodium sulfate. Remove the funnel after allowing it to drain.

Attach a solvent rinsed three ball macro-Snyder column to the KD apparatus and concentrate the extracts by evaporating the solvent on a hot water bath. Place the tip of the concentrating ampule into a boiling water bath. Tap the KD apparatus gently until the solvent begins to boil and the balls begin to "chatter" then lower the KD until the boiling water is at about the level of the 10 mL mark on the concentrating ampule. Adjust the vertical position of the apparatus and the water temperature to complete the concentration in 10 to 15 minutes. Remove the KD apparatus from the water bath and allow it to cool and drain. When the apparent volume of liquid reaches 1 mL, remove the KD apparatus, rinse down the Snyder column with 1 to 2 mL of methylene chloride and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and the KD flask, rinsing the ground glass joints with methylene chloride. Quantitatively transfer the extract to a 10 mL volumetric flask and bring to volume using methylene chloride. Transfer 1.0 mL to a screw top autosampler vial and deliver the remaining 9 mLs to the appropriate Semi-Vol personnel. If the sample is not to be shared with Semi-Vols the extract should be transferred to a 2 dram vial marked as the methylene chloride sample extract.

<u>Gel Permeation Chromatography (GPC) Clean Up</u>

Dilute 0.50 mL of the methylene chloride extract to a final volume of 10 mL in a volumetric flask. The diluted sample extract must be filtered into the input vials before running through the GPC. Place a disposable 13 mm, 0.45 um nylon syringe filter unit on the Leur-lock tip of a methylene chloride rinsed syringe. Place the tip of the filter unit into a methylene chloride rinsed sample input vial (15 mL screw top test tube) and pour 7 to 10 mL of the diluted extract into the syringe barrel. Insert the syringe plunger into the barrel and force the

sample extract through the filter into the input vial. Screw the input vial onto the input module of the GPC.

Place hexane rinsed sample collection vials (10 mL crimp top vials) in the sample collection module, be sure the position of the collection vial corresponds to the position of the input vial and that the collection vials are labeled with the corresponding sample number. Be sure all solvent reservoirs are full, the air is on, the pump is on, the pressure is set properly and the sample flow rate is correct. (See section XXX for proper GPC instrumental parameters.) Index through the run parameters and set the initial and terminal sample positions. Start the GPC. The GPC will load 5 mL of the sample extract onto the column for clean up.

After eluting the sample through the column, the extract is concentrated and is exchanged into hexane. The hexane extract is brought to a final volume of 5 mL and is transferred to the sample collection vial. Quantitatively transfer the hexane extract from the collection vial to a hexane rinsed 10 mL concentrating ampule. Rinse the collection vial three times with hexane and add the rinses to the ampule. Attach a hexane rinsed two ball micro-Snyder column to the ampule and concentrate the sample to less than 1 mL in the hot water bath. During the final concentration the inside wall of the micro-snyder must be rinsed down several times. It is critical that the extract not be allowed to boil dry. Bring the volume of the extract up to exactly 1 mL in the concentrating ampule, with hexane.

Alumina Clean up

Prepare an alumina column by adding 3 grams of activity III alumina to a glass wool plugged disposable pipet. Place the alumina column in the top of a hexane rinsed 10 mL concentrating ampule. Add 1 mL of acetone to the hexane extract in the original concentrating ampule. Transfer the hexane/acetone extract to the alumina column and allow to drain into the new 10 mL concentrating ampule. Rinse the concentrating ampule three times with hexane (approximately 1 mL aliquots) and add each rinse to the alumina column. Finally elute the alumina column with about 5 mL of hexane. Place a clean, hexane rinsed two ball micro-Snyder column on the concentrating ampule (with the cleaned up extract) and concentrate the extract to exactly 1 mL on a hot water bath. Transfer the 1 mL extract to an autosampler vial for analysis by GC. Be sure to mark the crimp top cap of the autosampler vial "SAVE" since this is all the sample. When the instrumental analysis is completed, the extract should be transferred to a screw top autosampler vial for storage.

5. Quality control

A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 30 grams of granular sodium sulfate in the same manner as the samples.

A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 30 grams of granular sodium sulfate with 800 uL of a pesticide standard mix. (For analytes and concentrations see section IV, D page 32.) The standard is then extracted in the same manner as the samples.

A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The spikes are prepared by spiking 30 grams of one sample with 800 uL of the pesticide standard mix, and then extracting in the same manner as the sample.

PCB/Pesticide Solid Extraction - Lab bench copy

I. Apparatus
   A. Balance
   B. 400 mL beakers (thick walled)
   C. 100 mL graduated cylinder
   D. Tekmar Ultrasonic Cell disrupter:
      Controller - 500 watt with pulsing capability,
      Disrupter horn - solid, 3/4 inch standard tip,
      Sound enclosure and lab jack
   E. Kuderna-Danish (KD) evaporative concentrator:
      10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
   F. Glass Moonie funnel - 20 mm
   G. Glass wool
   H. Hot water bath
   I. 10 mL volumetric flasks
   J. Volumetric pipets - various sizes
   K. Disposable pasteur pipets
   L. Alumina columns
   M. Boiling chips
   N. Teflon stir rods
   O. Autosampler vials with crimp top caps
   P. Screw top autosampler vials with teflon liners and lids
   Q. 2 Dram vials with teflon lined lids

II. Reagents
   A. Methylene chloride - optima grade
   B. Acetone - certified ACS
   NOTE: prepare a 1:1 methylene chloride/acetone mix
   C. Hexane - optima grade
   D. Sodium sulfate - granular, anhydrous, baked at 400°C for 24 hours
   E. Sodium sulfate - powdered, anhydrous, baked at 400°C for 24 hours
   F. Surrogate solution:
      1.0 mg/L DBC and 1.0 mg/L 2,4,5,6-tetrachloro-m-xylene in methanol
   G. Alumina (activity III)

III. Procedure
   A. All glassware should be cleaned with hot soapy (microsoap) water, rinsed with tap water, distilled water and a final rinse with acetone.
   B. Immediately before use all glassware should be solvent rinsed three times with methylene chloride.

PCB/Pesticide Solid Extraction - Lab bench copy
(continued)

C. The samples should be removed from the cooler and allowed to warm to ambient temperature before extracting.

D. Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially, composite samples. Discard any foreign objects such as sticks, leaves and rocks.

E. Weigh approximately 30 grams of sample to the nearest 0.1 g into a 400 mL beaker.

F. Add 60 grams of anhydrous, powdered sodium sulfate to the beaker and mix well.

NOTE: The sample should have a sandy texture at this point.

G. Immediately add 100 mL of 1:1 methylene chloride/acetone to the sample.

NOTE: The pH of the sample and the percent moisture should be determined. These tests are performed by the General Inorganinc Lab.

H. Place the beaker onto the lab jack in the ultrasonic cell disrupter sound enclosure.

I. Raise the lab jack to the point where the bottom surface of the tip of the horn is about 1/2 inch below the surface of the solvent but above the sediment layer.

J. Sonicate for 3 minutes using the 3/4 inch horn with the output control knob set at 10 and the mode switch on "pulse" and % duty cycle knob set at 50%.

NOTE: If using a dual controller, be sure both horn tips are submersed before turning on.

K. Assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask.

L. Add two to three boiling chips to the KD flask.

M. Plug a glass moonie funnel with a piece of glass wool and fill the funnel 3/4 full with baked granular sodium sulfate.

N. Rinse the sodium sulfate (in the funnel) three times with methylene chloride and allow to drain.

O. Place the moonie funnel on top of the KD apparatus.

P. Decant and filter the extract through the sodium sulfate into the KD apparatus.

NOTE: The funnel with the sodium sulfate acts as a drying column to retain any water included with the methylene chloride.

Q. Repeat the extraction procedure two times with two additional 100 mL portions of 1:1 methylene chloride/ acetone.

NOTE: Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean teflon stir rod.

R. Decant off the extract after each sonication.

PCB/Pesticide Solid Extraction - Lab bench copy
(continued)

S. After the final sonication and filtration, rinse the sodium sulfate with 1:1 methylene chloride/acetone and add the rinse to the KD apparatus, through the sodium sulfate.
T. Remove the funnel after allowing it to drain.
U. Attach a solvent rinsed three ball macro-Snyder column to the KD apparatus and concentrate the extracts by evaporating the solvent on a hot water bath.
V. Place the tip of the concentrating ampule into a boiling water bath. Tap the KD apparatus gently until the solvent begins to boil and the balls begin to "chatter" then lower the KD until the boiling water is at about the level of the 10 mL mark on the concentrating ampule. Adjust the vertical position of the apparatus and the water temperature to complete the concentration in 10 to 15 minutes.
W. Remove the KD apparatus from the water bath and allow it to cool and drain.
X. When the apparent volume of liquid reaches 1 mL, remove the KD apparatus and rinse down the Snyder column with 1 to 2 mL of methylene chloride.
Y. allow it to drain and cool for at least 10 minutes.
Z. Remove the Snyder column and the KD flask, rinsing the ground glass joints with methylene chloride.
AA. Quantitatively transfer the extract to a 10 mL volumetric flask and bring to volume using methylene chloride.
BB. Transfer 1.0 mL to a screw top autosampler vial and deliver the remaining 9 mLs to the appropriate Semi-Vol personnel.

NOTE: If the sample is not to be shared with Semi-Vols the extract should be transferred to a 2 dram vial marked sa the methylene chloride sample extract.

Gel Permeation Chromatography (GPC) Clean Up

A. Dilute 0.50 mL of the methylene chloride extract to a final volume of 10 mL in a volumetric flask.
B. The diluted sample extract must be filtered into the input vials before running through the GPC.
C. Place a disposable 13 mm, 0.45 um nylon syringe filter unit on the Leur-lock tip of a methylene chloride rinsed syringe.
D. Place the tip of the filter unit into a methylene chloride rinsed sample input vial (15 mL screw top test tube) and pour 7 to 10 mL of the diluted extract into the syringe barrel.
E. Insert the syringe plunger into the barrel and force the sample extract through the filter into the input vial.
F. Screw the input vial onto the input module of the GPC.

PCB/Pesticide Solid Extraction - Lab bench copy
(continued)

G. Place hexane rinsed sample collection vials (10 mL crimp top vials) in the sample collection module, be sure the position of the collection vial corresponds to the position of the input vial.
H. Be sure all solvent reservoirs are full, the air is on, the pump is on, the pressure is set properly and the sample flow rate is correct. (See section XXX for proper GPC instrumental parameters.)
I. Index through the run parameters and set the initial and terminal sample positions.
J. Start the GPC.
K. The GPC will load 5 mL of the sample extract onto the column for clean up.
L. After eluting the sample through the column, the extract is concentrated and is exchanged into hexane. The hexane extract is brought to a final volume of 5 mL and is transferred to the sample collection vial.
M. Quantitatively transfer the hexane extract from the collection vial to a hexane rinsed 10 mL concentrating ampule.
N. Rinse the collection vial three times with hexane and add the rinses to the ampule.
O. Attach a hexane rinsed two ball micro-Snyder column to the ampule and concentrate the sample to less than 1 mL in the hot water bath. During the final concentration the inside wall of the micro-snyder must be rinsed down several times.

NOTE: It is critical that the extract not be allowed to boil dry.

P. Bring the volume of the extract up to exactly 1 mL in the concentrating ampule, with hexane.

<u>Alumina Clean up</u>

A. Prepare an alumina column by adding 3 grams of activity III alumina to a glass wool plugged disposable pipet.
B. Place the alumina column in the top of a hexane rinsed 10 mL concentrating ampule.
C. Add 1 mL of acetone to the hexane extract in the original concentrating ampule.
D. Transfer the hexane/acetone extract to the alumina column and allow to drain into the new 10 mL concentrating ampule.
E. Rinse the concentrating ampule three times with hexane (approximately 1 mL aliquots) and add each rinse to the alumina column.
F. Finally elute the alumina column with about 5 mL of hexane.

PCB/Pesticide Solid Extraction - Lab bench copy
(continued)

G. Place a clean, hexane rinsed two ball micro-Snyder column on the concentrating ampule (with the cleaned up extract) and concentrate the extract to exactly 1 mL on a hot water bath.

H. Transfer the 1 mL extract to an autosampler vial for analysis by GC. Be sure to mark the crimp top cap of the autosampler vial "SAVE" since this is all the sample.

I. When the instrumental analysis is completed, the extract should be transferred to a screw top autosampler vial for storage.

IV. Quality control

A. A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 30 grams of granular sodium sulfate in the same manner as the samples.

B. A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 30 grams of granular sodium sulfate with 800 uL of a pesticide standard mix. (For analytes and concentrations see section IV, D page 32.) The standard is then extracted in the same manner as the samples.

C. A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The spikes are prepared by spiking 30 grams of one sample with 800 uL of the pesticide standard mix, and then extracting in the same manner as the sample.

A. Waste (oil) Extraction - Prep Code: P237.1
Reference Method: SW846-3500 (SW846-3580 modified)

1. Theory

Because of the high solubility of both the oil (waste) and the pesticides in hexane, the procedure used is a weight per unit volume dilution. After dilution of the sample into hexane clean up procedures are used to remove interferences.

2. Apparatus

2 Dram vials
vortex mixer
100 uL syringe
volumetric pipets
Alumina columns
disposable pipets
Autosampler vials with crimp top caps

3. Reagents

Hexane - optima grade
Acetone - certified ACS
Activity III Alumina
Surrogate solution:
10 mg/L DBC and 10 mg/L 2,4,5,6-tetrachloro-m-xylene in hexane

4. Procedure

Weigh out approximately 0.10 gram of sample into a 2 dram vial. Add 1 mL of hexane, cap and vortex. Add 100 uL of the surrogate solution to the sample. Add 1 mL of acetone to the 2 dram vial, cap and vortex.

NOTE: This may leave some suspended solids if the oil contained particulate. If the sample is an "oily soil" it should be prepped as indicated in SW846-3550 (sonication of solids, P236.1).

<u>Alumina Clean Up</u>

Prepare an alumina column by adding 3 grams of activity III alumina to a glass wool plugged disposable pipet. Place the alumina column in the top of a hexane rinsed 10 mL volumetric flask. Transfer the hexane/acetone extract to the alumina column and allow to drain into the 10 mL volumetric flask. Rinse the 2 dram vial three times with hexane (approximately 1 mL aliquots) and add each rinse to the alumina column. Finally elute the alumina column with about 5 mL of hexane. Bring the extract to a final volume of 10 mL in the volumetric flask. Transfer a 1 mL aliquot of the extract to an autosampler vial for analysis by GC. Transfer the remainder of the extract to a 2 dram vial for storage.

5. Quality control

A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by weighing out 0.100 grams of the clean oil standard and extracting in the same manner as the samples

A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 0.100 grams of clean oil with 100 uL of the pesticide standard mix for soils. (For analytes and concentrations see section IV, D page 32.) The standard is then extracted in the same manner as the samples.

A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The spikes are prepared by spiking 0.100 grams of the sample with 100 uL of the pesticide standard mix for soils, and then extracting in the same manner as the sample.

PCB Pesticide Oil Extraction - Lab bench copy

I. Apparatus
   A. 2 Dram vials
   B. vortex mixer
   C. 100 uL syringe
   D. volumetric pipets
   E. Alumina columns
   F. disposable pipets
   G. Autosampler vials with crimp top caps

II. Reagents
   A. Hexane - optima grade
   B. Acetone - certified ACS
   C. Activity III Alumina
   D. Surrogate solution:
      10 mg/L DBC and 10 mg/L 2,4,5,6-tetrachloro-m-xylene in hexane

IV. Procedure
   A. Weigh out approximately 0.10 gram of sample into a 2 dram vial.
   B. Add 1 mL of hexane, cap and vortex.
   C. Add 100 uL of the surrogate solution to the sample.
   D. Add 1 mL of acetone to the 2 dram vial, cap and vortex.
   NOTE: This may leave some suspended solids if the oil contained particulate. If the sample is an "oily soil" it should be prepped as indicated in SW846-3550 (sonication of solids, P236.1).

   Alumina Clean Up
   E. Prepare an alumina column by adding 3 grams of activity III alumina to a glass wool plugged disposable pipet.
   F. Place the alumina column in the top of a hexane rinsed 10 mL volumetric flask.
   G. Transfer the hexane/ acetone extract to the alumina column and allow to drain into the 10 mL volumetric flask.
   H. Rinse the 2 dram vial three times with hexane (about aliquots) and add each rinse to the alumina column.
   I. Finally elute the alumina column with about 5 mL of hexane.
   J. Bring the extract to a final volume of 10 mL in the volumetric flask.
   K. Transfer a 1 mL aliquot of the extract to an autosampler vial for analysis by GC.
   L. Transfer the remainder of the extract to a 2 dram vial for storage.

PCB/Pesticide Oil Extraction - Lab bench copy
(continued)

V. Quality control

A. A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by weighing out 0.100 grams of the clean oil standard and extracting in the same manner as the samples.

B. A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 0.100 grams of clean oil with 100 uL of the pesticide standard mix for soils. (For analytes and concentrations see section IV, D page 32.) The standard is then extracted in the same manner as the samples.

C. A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The spikes are prepared by spiking 0.100 grams of the sample with 100 uL of the pesticide standard mix for soils, and then extracting in the same manner as the sample.

III. GC/ECD Analysis Procedure

A. Theory

The PCB aroclors are mixtures of the various PCB congeners, each of which will elute from a chromatographic column at a characteristic retention time. Each aroclor has a unique chromatographic pattern that is representative of the congeners present in the aroclor. Comparison of the sample characteristics against the characteristics of calibration standards provides a means of identifying and quantitating any PCBs present in the sample. The two pesticides, toxaphene and technical grade chlordane, are pesticide mixes that have a characteristic pattern that allows for identification and quantitation.

The other pesticides that are tested for are single compounds that have a specific retention time under given instrumental conditions. Since these pesticides are identified by only one peak, a secondary run on a column of different polarity must be analyzed for confirmation. The pesticides are identified by comparison of the retention time of an eluting peak with the retention times of the analytes of interest in the calibration standard. In this analysis, the analytes are only reported if they can be identified on both the primary column and the confirmation column. For most analyses, the DB-608 megabore column is used as the primary column and the DB-5 capillary column is used for confirmation.

All calculations are based on an external calculation using calibration standards that are analyzed in the same analytical sequence as the samples. Using the concentration and areas of the standard peaks and the area of the sample peaks, a concentration in the sample extract can be determined. By adjusting the extract concentration for the sample volume and final extract volume, the concentration in the sample can be determine.

B. Method - reference SW846-8080

The hexane sample extracts are analyzed using Hewlett-Packard model 5880 or model 5890 gas chromatographs, with an electron capture detector (ECD). A J+W DB-608 megabore column is used for the primary analysis and a J+W DB-5 capillary column is used for the confirmation analysis. Each instrument is configured "dual channel" where two injection ports, two columns and two detectors are in the same instrument. This configuration allows the analysis of the primary and confirmation runs at the same time. An argon/methane mix (P-5) is used as the make-up gas, hydrogen is used as the carrier gas for the DB-5 columns and helium is used as the carrier gas for the DB-608 column. The following chromatographic conditions should be used:

1. Temperature program

	HP-5880	HP-5890
Initial value	130 °C	130 °C
Initial time	3.00 min	3.00 min
Level 1		
Prgm rate	5.00 °C/min	5.00 °C/min
Final value	200 °C	200 °C
Final time	0.00 min	0.00 min
Level 2		
Prgm rate	10.00 °C/min	10.00 °C/min
Final value	250 °C	250 °C
Final time	10.00 min	10.00 min
Level 3		
Prgm rate	25.00 °C/min	28.00 °C/min
Final value	275 °C	278 °C
Final time	0.00 min	0.00 min

2. Injector temperature = 175 °C

3. Detector temperature = 300 °C

4. Attenuation - varies with instrument and detector age

5. Threshold - varies with instrument and detector age

6. Peak width - varies with instrument

7. Gas flows

HP-5880 DB-5 column	
Septum purge	2 to 3 mL/min
Split vent	20 mL/min
Total flow	35 mL/min

HP-5890 DB-5 column	
Total	45 mL/min
Split	18 mL/min
Column	8.00 mL/min
Purge	2 to 3 mL/min

HP-5880 and HP-5890 DB-608 column	
Total	45 mL/min
Column	8.8 mL/min

Calibration standards for each analyte are prepared from EPA stock standards. On each PCB/Pesticide sequence the following calibration standards must be analyzed:

1. Evaluation Mixes - used to determine linearity (as %RSD) and to determine breakdown.

Analyte	Concentration EVAL A	EVAL B	EVAL C
Aldrin	0.010 mg/L	0.020 mg/L	0.050 mg/L
Endrin	0.020 mg/L	0.040 mg/L	0.100 mg/L
4,4'-DDT	0.020 mg/L	0.040 mg/L	0.100 mg/L
DBC	0.020 mg/L	0.040 mg/L	0.100 mg/L

2. Individual Mixes - used for calibrating and determining the consistency of response from beginning to ending of run (as %D).

IND A		IND B	
Analyte	conc.	Analyte	conc.
gamma-BHC	0.0125	alpha-BHC	0.0125
Heptachlor	0.025	beta-BHC	0.025
Aldrin	0.025	delta-BHC	0.025
Hept.Epoxide	0.025	Aldrin	0.025
Endosulfan I	0.025	g.Chlordane	0.025
Dieldrin	0.025	a.Chlordane	0.025
Endosulfan II	0.050	4,4'-DDE	0.050
4,4'-DDT	0.050	Endrin	0.025
End. Aldehyde	0.025	4,4'-DDD	0.050
Methoxychlor	0.250	Enso.Sulfate	0.050
DBC	0.10	End.Ketone	0.050
		DBC	0.10

3. Toxaphene 0.500 mg/L and DBC 0.10 mg/L

4. Aroclor 1016 0.500 mg/L and DBC 0.10 mg/L

5. Aroclor 1221 0.500 mg/L and DBC 0.10 mg/L

6. Aroclor 1232 0.500 mg/L and DBC 0.10 mg/L

7. Aroclor 1242 0.500 mg/L and DBC 0.10 mg/L

8. Aroclor 1248 0.500 mg/L and DBC 0.10 mg/L

9. Aroclor 1254 0.500 mg/L and DBC 0.10 mg/L

10. Aroclor 1260 0.500 mg/L and DBC 0.10 mg/L

Each analytical sequence must start with all of the calibration standards. There should always be a calibration standard between every 5 samples (the 5 samples representing either a sample, SPI or DPS). Each sequence must have at least one BLA, ICV, SPI and DPS. The calibration standards should be alternated within the run as indicated in the following sequence. Each sequence must end with both an IND A and an IND B. The sequence may continue as long as it remains within the calibration acceptance limits. If at any point within the run the standards are outside of the QA/QC limits, the run must be restarted at the last standard that is in control.

The analytical sequence that should be followed is:

Hexane Blank
EVAL A
EVAL B
IND A
IND B
Toxaphene
Aroclor 1016
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
BLA 02
ICV 02
Sample #1
Sample #1 SPI02
Sample #1 DPS02
EVAL B
5 samples
IND A
5 samples
EVAL B
5 samples
IND B
5 samples
EVAL B
|
|
IND A
IND B

If any of the other aroclors, or if technical chlordane is present in a sample, a standard for that particular analyte must also be analyzed either during or at the end of the run.

IV. Quality Assurance/Quality Control (QA/QC) - analytical

Quality control procedures described by the EPA in Vol.49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness and representativeness of its data are known and documented. A start-up test of the instrument in use is done to establish the laboratory's ability to set up and operate the analytical instrumentation and procedures. The purpose is to prove that the compounds of interest can be detected under the parameters set forth and that the analyst can identify the compounds. This test includes a detection limit determination that is performed when a new analysis is first begun and is repeated periodically. Both instrument and method detection limits are determined at this time.

To further assure the representativeness of data produced for the PCB/Pesticide analyses, internal QA/QC is routinely performed on all types of sample matrices. This QA/QC includes analytical blanks, standards, matrix spikes and matrix spike duplicates.

A. Method (prep) Blanks - BLA02
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run)
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   Acceptable limit: Below detection limit (BDL)

   If a compound of interest is present in the method blank, any samples with that compound in them that were prepped on the same day must be re-prepped.

B. Method (prep) Standard - (ICV02)
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run)
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   Results for the Standard are reported as percent recovery using the following formula:

$$\%REC = \frac{\text{Standard Result (concentration)}}{\text{True Value}} \times 100$$

   Acceptable limit: see table on page 32.

C. Matrix Spike (SPI02 or MS)
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run)
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   Results for the Matrix Spike are reported as percent recovery using the following formula:

$$\%REC = \frac{\text{Matrix Spike Result - Sample result}}{\text{True Value}} \times 100$$

   Acceptable limit: see table below

D. Matrix Spike Duplicate (DPS02 or MSD)
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run)
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   Results for the Matrix Spike Duplicate are reported as percent recovery and percent reproducablility using the following formulas:

$$\%REC = \frac{\text{Matrix Spike Result - Sample result}}{\text{True Value}} \times 100$$

$$\%RPD = \frac{2\,|\,D1 - D2\,|}{D1 + D2} \times 100 \qquad D1 = \%REC\ SPI \quad D2 = \%REC\ DPS$$

   Acceptable limit: see table below

The following table lists the spiking solutions used and the acceptance limits for pesticide spikes:

Analyte	Spike Standard* waters	Spike Standard* soils	Acceptance limits Waters %REC	Waters %RPD	Soils %REC	Soils %RPD
gamma-BHC	0.20	2.0	56-123	15	46-127	50
Heptachlor	0.20	2.0	40-131	20	35-130	31
Aldrin	0.20	2.0	40-120	22	34-132	43
Dieldrin	0.50	2.0	52-126	18	31-134	38
Endrin	0.50	2.0	56-121	21	42-139	45
4,4'-DDT	0.50	2.0	38-127	27	23-134	50

*Concentration of spiking solution in mg/L.

E. Continuing Calibration Verification - CCV

The CCV is run during each analytical sequence to show consistency in response from beginning to end. A percent deviation is calculated between the beginning IND mixes and any subsequent IND mix. The percent deviation is calculated using the following equation:

$$\%DEV = \frac{\text{Beginning Response} - \text{Ending Response}}{\text{Beginning Response}} \times 100$$

Acceptance limit: For the Primary channel the %DEV must be less than 15% for all analytes and for the confirmation channel the %DEV must be less than 20% for all analytes.

F. Linearity

The linearity of the calibration range is calculated using the response factors of the three EVAL mixes at the beginning of the run. The linearity is checked as the % relative standard deviation (%RSD) of the response factors. The acceptable limit for the %RSD is 10%. If this limit is not met, a calibration curve must be established for the calculations.

G. Breakdown

In the presence of high boiling residue, or active sites, in the injection port both Endrin and 4,4'-DDT will "breakdown". Endrin will undergo a thermal isomerization into its breakdown products endrin aldehyde and endrin ketone. The pesticide 4,4'-DDT will form its breakdown products, 4,4'-DDE and 4,4'-DDD, by loosing Cl or HCl. As an indication of the condition of the injection port, the breakdown products must be calculated on all EVAL B mixes in the run. The breakdown is calculated using the following equations.

Breakdown is calculated using the peak areas as follows:

$$\%Endrin = \frac{\text{Endrin Aldehyde} + \text{Endrin Ketone}}{\text{Endrin} + \text{Endrin Aldehyde} + \text{Endrin Ketone}} \times 100$$

$$\%\ DDT = \frac{DDE + DDD}{DDT + DDE + DDD} \times 100$$

$$\%Combined = \frac{\text{End Ald} + \text{End Ket} + DDE + DDD}{\text{End} + \text{End Ald} + \text{End Ket} + DDT + DDE + DDD} \times 100$$

Acceptance limit: The combined breakdown must be less than 20%

H. Surrogate recovery

The surrogate recovery must be calculated for each sample, BLA02, ICV02, SPI02, and DPS02. The surrogate recovery should be calculated for the DBC unless interferences prohibit its use. In the case where the DBC can not be used, the TCX may be used for surrogate recovery. The surrogate recovery is calculated by comparing the sample surrogate extract concentration with the expected concentration.

Acceptance limits:

Waters	34-123%
Soils	23-146%

I. Data review

All data generated must be reviewed by the GC group leader or a designee. The data must be reviewed for completeness and accuracy before being turned in for data entry. The reviewer is responsible for making sure all relevant information has been recorded correctly and that all QA/QC requirements have been met. The reviewer should be sure all sample calculations are complete and are accurately reported. After review of an analytical run, all run sheets should be initialed and dated, as well as the run folder.

NOTE: No one can review their own data.

V. Calculations

A. Theory

Using an external standard calculation with the calibration standards on each analytical run, a sample extract concentration can be determined. Using the extract concentration, the initial weight or volume, the final volume and any dilution factors, the concentration in the sample can be determined. Identification of the aroclors and the multi-peak pesticides (technical grade chlordane and toxaphene) is by retention time of major peaks and pattern recognition. The major peaks must be present and in the same proportion as the same peaks in the standard. The single peak pesticides are identified by calculating a retention time window. If the analyte is present within the window a concentration is calculated. An analyte can not be reported without confirmation on a column of different polarity

B. Calculations - Equations

1. Retention time windows

For the DB-5 capillary columns the retention time window is calculated as the retention time of the beginning standard plus or minus 15%. For the DB-608 megabore column the retention time window is calculated as the retention time of the beginning standard plus or minus three times the standard deviation in retention time (as determined on the recalibration run).

The recalibration run is set up as a 72 hour sequence with all medium level standards at the beginning, the middle and the end of the run. The standard deviation in the retention time for each analyte is calculated using the retention times for the three medium level standards. If any peaks are present within the retention time window of the primary channel, the analyte is tentatively identified and a sample concentration is calculated. If the analyte that was identified is above the detection limit, then it must be confirmed. An analyte is confirmed if it is identified within the retention time window of the confirmation run.

2. Response factor

Response factors are calculated for each analyte. For multi-peak analytes at least five peaks areas are summed for calculating the response factor.

$$\text{Resp. Factor} = \frac{\text{concentration of standard}}{\text{area (area sum) of standard}}$$

3. Extract concentration

After identifying a multi-peak analyte an area sum is calculated using the same peaks as were used in the calibration standard. For single peak analytes the area of the peak is determined. The extract concentration is calculated using the following equations:

Extr. Conc = (area sum of analyte) X (Resp. Factor) or
Extr. Conc = (area of analyte) X (Resp. Factor)

4. Sample concentration

Using the extract concentration, the concentration in the sample is determined using the following equation:

$$\text{Sample Conc.} = \frac{\text{(Extr.Conc.) X (Final Volume)}}{\text{Initial Weight or volume}}$$

If the sample had to be concentrated or diluted to be within the linear calibration range, the sample concentration must be multiplied by any dilution factor and a comment must be added to the run sheet.

VI. Interferences/Troubleshooting

A. Interferences

Most of the interferences should be removed by the clean up procedures indicated in the extraction procedures. If the normal clean up steps are not sufficient further clean up steps or dilutions may be necessary. Contamination can occur very readily in this test, especially during the extraction stages. It is extremely important that all glassware and apparatus (pipets, caps, syringes and vials) are clean before use. If precautions are followed during the extraction, the risk of interferences affecting the instrumental analysis will be at a minimum.

Some of the more common interferences are the phthalate compounds. In order to minimize this interference, plastics should not be used for the sample containers, the extraction procedure nor the extract storage. All reagents should be bought in glass containers. Pre-baking of the sodium sulfate will also reduce the chances of interferences. The use of GPC clean up for solid samples helps to reduce amount of interference caused by high boiling point and high molecular weight compounds. Another possible interference is from sulfur containing compounds. This interference can be eliminated by a sulfur clean up with mercury (see section XXX page XXX for method).

B. Troubleshooting

Troubleshooting is most commonly associated with the instrumental analyses. The upkeep of the instruments through routine instrument maintenance should help to reduce the amount of instrument down time. Some things to watch for as an indication of instrument problems are:

1. Inconsistent injections
2. Poor baselines
3. Retention time shifts
4. Peak widening
5. A change in sensitivity
6. Increase in breakdown products

At the first sign of any of these problems the instrument should be checked and steps should be taken to correct the problems.

VII. Safety Precautions

Because the contents of the samples are unknown, they should be treated with caution. Protective equipment such as safety glasses, a lab coat and gloves should be worn when prepping any sample. All liquid/liquid extractions should be performed in a fume hood with the sash pulled down as low as possible. The evaporation of the solvents, on a hot water bath, should also be performed in a fume hood. There is always a possibility that the KD apparatus may build up enough pressure to break while concentrating the extract, therefore all glassware should be checked carefully before use for any scratches or nicks that may provide a breakage point.

VIII. Clean up and Disposal

After the extraction of samples all reusable glassware, including separatory funnels, volumetrics, glass funnels, etc. are to be solvent rinsed and the rinse discarded into an appropriate waste container. The glassware should then be washed with hot soapy water, tap water rinsed, DI water rinsed, acetone rinsed and then allowed to air dry. Disposable pipets, tongue blades, disposable gloves and waste solvents should each be placed in the appropriately labeled waste containers for disposal at a later time.

After extraction, sample extracts (2 dram vials or screw top autosampler vial) are to be logged into the sample extract cooler and stored. The length of the storage time varies according to the submitters' requirements. Normally extracts are kept for at least 3 months before disposal. All samples should be returned to the sample storage coolers when the extraction is completed. All completed soil samples are disposed of by "Lab Pack", or are returned to the submitter. Extra water samples, that are non-detected for the analytes of interest are disposed of by flushing them down the sink drain with copious amounts of tap water.

Revision Date: October 23, 1990

CHLORINATED HERBICIDE ANALYSIS BY GC ECD

EMS Test Codes: 0253.1 or 0253.2 (for TCLP herbicides)
Method Quote: SW846-8150

Referenced Procedures
Methods: SW846-8150 and SW846-3590 (proposed)

I. Introduction:

This method is used to analyze for solvent extractable chlorinated acid herbicides. The herbicides are solvent extracted from the sample matrix and are then esterified before analysis. The analysis is performed by capillary gas chromatography with an electron capture detector. The instruments being used presently are Hewlett-Packard GCs (Model 5880 and Model 5890) with J+W DB-5 capillary columns and J+W DB-608 megabore columns. In most cases the DB-5 column is used as the primary column for identification and quantitation, while the DB-608 is used for confirmation if needed.

A. Tests - 0253.1 or 0253.2 - for analyte list see table below
B. Method Detection Limit - see table below

Analyte List and Detection Limits

	Method Det.Limits	Normal Det. limits*	
Analyte	waters (mg/L)	waters (mg/L)	solids(mg/Kg)
2,4-D	0.0012	0.01	0.2
2,4-DB	0.00091		
2,4,5-T	0.00020	0.001	0.02
2,4,5,-TP (Silvex)	0.00017	0.001	0.02
Dalapon	0.0058		
Dicamba	0.00027		
Dichloroprop	0.00065		
Dinoseb	0.00007		
MCPA	0.249		
MCPP	0.192		

* Routine analysis is only for Silvex, 2,4-D and 2,4,5-T.

C. Containers - All samples should be submitted in glass containers with teflon lined caps. Plastic containers should be avoided if at all possible. Waters should be submitted in a 1 liter amber glass bottle and should be completely filled. Solid samples should be submitted in a 250 mL wide mouth bottle and should contain at least 30 grams of sample. The methods require a matrix spike and a matrix spike duplicate at a frequency of 10% of the samples, therefore extra sample should be included to accomodate this requirement.

SOP Correction FORM

HERITAGE LABORATORIES, INC

SOP Number: OLD FORMAT

SOP Title: Chlorinated Herbicide Analysis by GC ECD

Page #: 1, 2, 9, 25

Requested by : Lisa Jackson Date: 1-5-94

Correction: SW846 - 8150 changed to SW 846-8150A

Reason (if applicable): Updated Method Cited

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager Signature: Gary A. Klingfa Date: 1/6/94

100892

D. Preservatives - none
E. Holding times
Waters: 7 days from sampling (5 days from receipt)
Solids: 14 days from sampling (12 days from receipt)
NOTE: Samples should be submitted to the lab within 24 hours of sampling to assure extraction within holding time.
F. Extract holding time - 14 days

II. Extraction Procedures:

The extraction procedure used is dependent on the sample matrix and the requirements of the client. For water samples either a liquid/liquid extraction or a solid phase extraction may be used. Solid samples must be solvent extracted by liquid/solid extraction, unless done as a leachate (for TCLP).

A. **Waters - Liquid/Liquid Extraction - P201.4**
Reference Method: SW846-8150

1. Theory

The herbicide esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography.

2. Apparatus

250 mL Erlenmeyer flasks with 24/40 ground glass joints
125 mL Erlenmeyer flasks
500 mL Graduated cylinder
500 mL Beakers
1000 mL Separatory funnels
250 mL Separatory funnels
Kuderna-Danish (KD) evaporative concentrator:
10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
Boiling chips
Water bath
Glass wool - acid washed and ether rinsed

3. Reagents

1:1 Sulfuric acid
Hydrochloric acid
37% aqueous Potassium hydroxide
Ethyl ether
Methyl-tert-butyl ether
Sodium sulfate - acid washed and ether rinsed

4. Procedure

All glassware should be washed with hot soapy water, acid rinsed, acetone rinsed and allowed to dry. It is imperative that soap be completely removed from all glassware.

Shake the sample and quantitatively transfer 250 mL of into a 1000 mL separatory funnel, using an acid washed glass graduated cylinder. Acidify the sample with 1:1 sulfuric acid and check with with alkacid paper to verify acidity of the sample. Add 100 uL of the 2-bromobenzoic acid used as a surrogate. Add 100 mL of ethyl ether to the graduated cylinder, rinsing the cylinder and pouring the ether into the separatory funnel. Shake the funnel vigorously for 2 minutes, venting to release pressure as needed. Do this only in a fume hood.

NOTE: The ether will build up a lot of pressure, frequent venting is necessary!

Support the separatory funnel in a ring stand and allow the ether layer to separate from the water phase for approximately 5 minutes. (The ether is the top layer.) Drain the water layer back into the graduated cylinder, and then collect the ether in 250 mL acid washed ground glass erlenmeyer flask. Extract the sample two more times with 30 mL of ether, adding the two extracts to the erlenmeyer flask.

Pipet approximately 10 mL of 30% potassium hydroxide into the flask, check the pH with alkacid paper to assure it is basic. Add 2 to 3 acid washed boiling chips and about 30 mL of distilled water to the flask. Swirl the flask to mix. Attach a three ball macro-Snyder column to the flask and place the flask on a hot plate turned on low heat to evaporate the ether under a hood. Continue to heat the extract for a total of one hour. Remove the flask from the hot plate and allow the sample to cool completely.

After the sample has cooled, remove the snyder column and transfer the sample to a 250 mL acid washed separatory funnel. Extract the sample one time with 50 mL of ethyl ether and discard the ether layer. Acidify the sample with 1:1 sulfuric acid (approximately 10 mL) and transfer the sample back to the 250 mL separatory funnel. Allow the sample to cool. Extract the sample three times with ethyl ether using 40 mL, 20 mL and 20 mL aliquots. Collect the extracts into a clean, acid washed, dry 125 mL Erlenmeyer flask containing acid washed, ether rinsed, anhydrous, baked sodium sulfate (approximately one inch or to the 50 ml mark). Cover the flask with aluminum foil and allow to sit for at least 2 hours. This step is a drying step that removes any water from the ethyl ether extract.

NOTE: If a large batch is being extracted, it is best to get all samples to this point and allow them to dry overnight.

After the sample extract has dried for at least two hours, assemble a KD concentrator by attaching a 10 mL acid washed concentrating ampule to a 500 mL acid washed KD flask. Add two to three acid washed boiling chips to the KD flask. Quantitatively transfer the sample extract to the KD flask. Rinse the sodium sulfate three times with ethyl ether using 20 mL rinses, and add the rinses to the KD flask. Be sure to break up any 'clumps' of sodium sulfate in the erlenmeyer flask while rinsing. Attach an ether rinsed three ball macro-Snyder column to the KD apparatus. Concentrate the extract by evaporating on a hot water bath. Place the tip of the ampule into the boiling water bath and tap the KD appartus gently until the solvent begins to boil and the balls begin to 'chatter'. Lower the KD apparatus until the boiling water is at about the level of the 10 mL mark on the concentrating ampule. Concentrate the sample extract to about 2 mL. Remove the apparatus from the bath, rinse the snyder column with about 2 mL of methyl-t-butyl ether (MTBE) and allow it to drain and cool. Remove the macro-Snyder column and the KD flask from the ampule, and add approximately 5 mL of MTBE. Attach an ether rinsed micro-Snyder column to the ampule. Pre-elute the micro-Snyder column with MTBE and carefully concentrate the sample to 1 mL on the hot water bath. Remove the ampule and allow it to cool. The sample is now ready for derivatization using diazomethane as described on page 105.

5. Quality control

Calibration standards must be prepared by adding 1 mL of the herbicide standard solution to an ether rinsed ampule. Add approximately 5 mL of MTBE and 2 to 3 acid washed boiling chips to the ampule. Concentrate the calibration standard to 1 mL on the hot water bath. The standard is now ready for derivatization using diazomethane.

NOTE: Record the calibration standard in the standard log book, and assign it a calibration standard number.

A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 300 mL of DI water in the same manner as the samples.

A prep standard (ICV02) should be prepared at the beginning of each prep page,—thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 300 mL of DI water with 1 mL of the herbicide spiking solution. The standard is then extracted in the same manner as the samples.

A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide enough sample to accomodate the SPI and DPS requirements for each group of ten samples. The matrix spikes are prepared by spiking 300 mL of the sample with 1 mL of the herbicide spiking solution, and then extracting in the same manner as the samples.

HERBICIDE LIQUID/LIQUID EXTRACTION - Lab bench copy

I. Apparatus
   A. 250 mL Erlenmeyer flasks with 24/40 ground glass joints
   B. 125 mL Erlenmeyer flasks
   C. 500 mL Graduated cylinder
   D. 500 mL Beakers
   E. 1000 mL Separatory funnels
   F. 250 mL Separatory funnels
   G. Kuderna-Danish (KD) evaporative concentrator:
      10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
   H. Boiling chips
   I. Water bath
   J. Glass wool - acid washed and ether rinsed

II. Reagents
   A. 1:1 Sulfuric acid
   B. Hydrochloric acid
   C. 37% aqueous Potassium hydroxide
   D. Ethyl ether
   E. Methyl-tert-butyl ether
   F. Sodium sulfate - acid washed and ether rinsed

III. Procedure
   A. All glassware should be acid washed solvent rinsed with acetone and dry. It is imperitave that soap be completely removed from all glassware.
   B. Shake the sample and quantitatively transfer 300 mL of into a 1000 mL separatory funnel, using an acid washed glass graduated cylinder.
   C. Acidify the sample with 1:1 sulfuric acid and check with with alkacid paper to verify acidity of the sample.
   D. Add 100 uL of the 2-bromobenzoic acid used as a surrogate.
   E. Add 100 mL of ethyl ether to the graduated cylinder, rinsing the cylinder and pouring the ether into the separatory funnel.
   F. Shake the funnel vigorously for 2 minutes, venting to release pressure as needed.
   NOTE: Do this only in a <u>fume hood</u>.
   NOTE: The ether will build up a lot of pressure, frequent venting is necessary!
   G. Support the separatory funnel in a ring stand and allow the ether layer to separate from the water phase for approximately 5 minutes.
   NOTE: The ether is the <u>top</u> layer.
   H. Drain the water layer back into the graduated cylinder, and then collect the ether in 250 mL acid washed ground glass erlenmeyer flask.

HERBICIDE LIQUID/LIQUID EXTRACTION - Lab bench copy

I. Extract the sample two more times with 30 mL of ether, adding the two extracts to the erlenmeyer flask.

J. Pipet approximately 10 mL of 30% potassium hydroxide into the flask, add 2 to 3 acid washed boiling chips and 30 mL of distilled water to the flask.

K. Swirl the flask to mix. Check the pH with alkacid paper to assure it is basic.

L. Attach a three ball macro-Snyder column to the flask and place the flask on a hot plate to evaporate the ether under a hood.

M. Continue to heat the extract for a total of one hour.

N. Remove the flask from the hot plate and allow the sample to cool completely.

O. After the sample has cooled, remove the snyder column and transfer the sample to a 250 mL acid washed separatory funnel.

P. Extract the sample one time with 50 mL of ethyl ether and discard the ether layer.

Q. Acidify the sample with 1:1 sulfuric acid (approximately 10 mL), check the pH with alkacid paper, and transfer the sample to a 250 mL separatory funnel.

R. Allow the sample to cool.

S. Extract the sample three times with ethyl ether using 40 mL, 20 mL and 20 mL.

T. Collect the extracts into a clean, acid washed, dry 125 mL Erlenmeyer flask containing acid washed, anhydrous, baked sodium sulfate (approximately one inch or to the 50 ml mark).

U. Cover the flask with aluminum foil and allow to sit for at least 2 hours. This step is a drying step that removes any water from the ethyl ether extract.

NOTE: If a large batch is being extracted, it is best to get all samples to this point and allow them to dry overnight.

V. After the sample extract has dried for at least two hours, assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask.

W. Add two to three acid washed boiling chips to the KD flask.

X. Quantitatively transfer the sample extract to the KD flask.

Y. Rinse the sodium sulfate three times with ethyl ether using 20 mL rinses, and add the rinses to the KD flask.

NOTE: Be sure to break up any 'clumps' of sodium sulfate in the erlenmeyer flask while rinsing.

Z. Attach an ether rinsed three ball macro-Snyder column to the KD apparatus.

AA. Concentrate the extract by evaporating on a hot water bath.

BB. Place the tip of the ampule into the boiling water bath and tap the KD appartus gently until the solvent begins to boil and the balls begin to 'chatter'.

CC. Lower the KD apparatus until the boiling water is at about the level of the 10 mL mark on the concentrating ampule.

DD. Concentrate the sample extract to about 2 mL.

EE. Remove the apparatus from the bath, rinse the snyder column with about 2 mL of methyl-t-butyl ether (MTBE) and allow it to drain and cool.

FF. Remove the macro-Snyder column and the KD flask from the ampule, and add approximately 5 mL of MTBE.

GG. Attach an ether rinsed micro-Snyder column to the ampule.

HH. Pre-elute the micro-Snyder column with MTBE and carefully concentrate the sample to 1 mL on the hot water bath.

II. Remove the ampule and allow it to cool.

JJ. The sample is now ready for derivatization using diazomethane.

IV. Quality control

A. Calibration standards must be prepared by adding 1 mL of the herbicide standard solution to an ether rinsed ampule. Add approximately 5 mL of MTBE and 2 to 3 acid washed boiling chips to the ampule. Concentrate the calibration standard to 1 mL on the hot water bath. The standard is now ready for derivatization using diazomethane.
NOTE: Record the calibration standard in the standard log book, and assign it a calibration standard number.

B. A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 300 mL of DI water in the same manner as the samples.

C. A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 300 mL of DI water with 1 mL of the herbicide spiking solution. The standard is then extracted in the same manner as the samples.

D. A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide enough sample to accomodate the SPI and DPS requirements for each group of ten samples. The matrix spikes are prepared by spiking 300 mL of the sample with 1 mL of the herbicide spiking solution, and then extracting in the same manner as the samples.

B. Soil Extraction - P201.4
Reference Method: SW846-8150

1. Theory

The herbicides are solvent extracted from the solid sample. The herbicide esters are then hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography.

2. Apparatus

32 oz. wide mouth glass jar (oil & grease) with a teflon lined lid
250 mL Erlenmeyer flasks with 24/40 ground glass joints
125 mL Erlenmeyer flasks
500 mL Graduated cylinder
400 mL Beaker
1000 mL Separatory funnels
250 mL Separatory funnels
Kuderna-Danish (KD) evaporative concentrator:
10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
Boiling chips
Water bath
Glass wool - acid washed and ether rinsed

3. Reagents

1:1 Sulfuric acid
Hydrochloric acid
37% aqueous Potassium hydroxide
Ethyl ether
Methyl-tert-butyl ether
Sodium sulfate - acid washed and ether rinsed
Washed sand (for blanks and standards)

4. Procedure

Obtain a homogenous sample by either using a sampling tube or by kneeding the sample. Weigh out approximately 10 grams of soil (to the nearest 0.1 gram) into a foil pan. Transfer the sample to an acid washed oil & grease jar and add approximately 200 mL of acidified DI water. Add 100 mL of ethyl ether to the jar. Shake for 2 minutes, venting frequently.

NOTE: It is important to vent the jar frequently because the ether will build up pressure.

Allow the solids to settle out. Transfer the liquid phases to an acid rinsed 400 mL beaker, then pour into an acid-rinsed separatory funnel. When the phase separation

is complete, drain the lower water layer back into the oil & grease jar. Drain the upper ether layer into a 250 mL erlenmeyer flask with a ground glass joint. Add about 15 mL of 37% potassium hydroxide and 6 acid washed boiling chips to the erlenmeyer flask. Check the pH with alkacid paper to assure the extract is basic. Repeat the ether extraction twice more with 50 mL portions of ether. After the last extraction, rinse down the walls of the separatory funnel into the erlenmeyer flask using DI water. Add about 30 mL of DI water to the erlenmeyer to flask. Attach a three ball macro-Snyder column to the flask and place the flask on a hot plate turned on medium heat to evaporate the ether under a hood. Continue to heat the extract for a total of one hour. Remove the flask from the hot plate and allow the sample to cool completely.

After the sample has cooled, remove the snyder column and transfer the sample to a 250 mL acid washed separatory funnel. Extract the sample one time with 50 mL of ethyl ether and discard the ether layer. Acidify the sample with 1:1 sulfuric acid (approximately 10 mL), check the pH to assure the sample is acidic. Transfer the sample to a 250 mL separatory funnel. Allow the sample to cool. Extract the sample three times with ethyl ether using 40 mL, 20 mL and 20 mL. Collect the extracts into a clean, ether rinsed, acid washed, dry 125 mL Erlenmeyer flask containing acid washed, anhydrous, baked sodium sulfate (approximately one inch or to the 50 ml mark). Cover the flask with aluminum foil and allow to sit for at least 2 hours. This step is a drying step that removes any water from the ethyl ether extract.

NOTE: If a large batch is being extracted, it is best to get all samples to this point and allow them to dry overnight.

After the sample extract has dried for at least two hours, assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask. Add two to three acid washed boiling chips to the KD flask. Quantitatively transfer the sample extract to the KD flask. Rinse the sodium sulfate three times with ethyl ether using 20 mL rinses, and add the rinses to the KD flask. Be sure to break up any 'clumps' of sodium sulfate in the erlenmeyer flask while rinsing. Attach an ether rinsed three ball macro-Snyder column to the KD apparatus. Concentrate the extract by evaporating on a hot water bath. Place the tip of the ampule into the boiling water bath and tap the KD appartus gently until the solvent begins to boil and the balls begin to 'chatter'. Lower the KD apparatus until the boiling water is at about the level of the 10 mL mark on the concentrating ampule. Concentrate the sample extract to about 2 mL. Remove the apparatus from the bath, rinse

the snyder column with about 2 mL of methyl-t-butyl ether (MTBE) and allow it to drain and cool. Remove the macro-Snyder column and the KD flask from the ampule, and add approximately 5 mL of MTBE. Attach an ether rinsed micro-Snyder column to the ampule. Pre-elute the micro-Snyder column with MTBE and carefully concentrate the sample to 1 mL on the hot water bath. Remove the ampule and allow it to cool. The sample is now ready for derivatization using diazomethane as described on page 105.

5. Quality control

Calibration standards must be prepared by adding 1 mL of the herbicide standard solution to an ether rinsed ampule. Add approximately 5 mL of MTBE and 2 to 3 acid washed boiling chips to the ampule. Concentrate the calibration standard to 1 mL on the hot water bath. The standard is now ready for derivatization using diazomethane.

NOTE: Record the calibration standard in the standard log book, and assign it a calibration standard number.

A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The blank is prepared by extracting 10 grams of washed sand in the same manner as the samples.

A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The standard is prepared by spiking 10 grams of washed sand with 1 mL of the herbicide spiking solution. The standard is then extracted in the same manner as the samples.

A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide enough sample to accomodate the SPI and DPS requirements for each group of ten samples. The matrix spikes are prepared by spiking 10 grams of the sample with 1 mL of the herbicide spiking solution, and then extracting in the same manner as the samples.

HERBICIDE SOLID EXTRACTION-- Lab bench copy

I. Appararus
   A. 32 oz. wide mouth glass jar (oil & grease) with a teflon lined lid
   B. 250 mL Erlenmeyer flasks with 24/40 ground glass joints
   C. 125 mL Erlenmeyer flasks
   D. 500 mL Graduated cylinder
   E. 400 mL Beaker
   F. 1000 mL Separatory funnels
   G. 250 mL Separatory funnels
   H. Kuderna-Danish (KD) evaporative concentrator: 10 mL concentrating ampule, 500 mL KD evaporating flask, three ball macro-Snyder column, and two ball micro-Snyder column
   I. Boiling chips
   J. Water bath
   K. Glass wool - acid washed and ether rinsed

II. Reagents
   A. 1:1 Sulfuric acid
   B. Hydrochloric acid
   C. 37% aqueous Potassium hydroxide
   D. Ethyl ether
   E. Methyl-tert-butyl ether
   F. Sodium sulfate - acid washed and ether rinsed
   G. Washed sand (for blanks and standards)

III. Procedure
   A. Obtain a homogenous sample by either using a sampling tube or by kneeding the sample.
   B. Weigh out approximately 10 grams of soil (to the nearest 0.1 gram) into a foil pan.
   C. Transfer the sample to an acid washed oil & grease jar.
   D. Add approximately 200 mL of acidified DI water.
   E. Add 100 mL of ethyl ether to the jar.
   F. Shake for 2 minutes, venting frequently.
   NOTE: It is important to vent the jar frequently because the ether will build up pressure.
   G. Allow the solids to settle out.
   H. Transfer the liquid phases to an acid rinsed 400 mL beaker, then pour into an acid-rinsed 1000 mL separatory funnel.
   I. When the phase separation is complete, drain the lower water layer back into the oil & grease jar.
   J. Drain the upper ether layer into a 250 mL erlenmeyer flask with a ground glass joint.
   K. Add about 15 mL of 37% potassium hydroxide and 6 acid washed boiling chips to the erlenmeyer flask.
   L. Repeat the ether extraction twice more with 50 mL portions of ether.

HERBICIDE SOLID EXTRACTION - Lab bench copy

M. After the last extraction, rinse down the walls of the separatory funnel into the erlenmeyer flask using DI water.
N. Add enough DI water to the erlenmeyer to have about 1/4 inch deep in the flask.
O. Attach a three ball macro-Snyder column to the flask and place the flask on a hot plate turned on medium heat to evaporate the ether under a hood.
P. Continue to heat the extract for a total of one hour.
Q. Remove the flask from the hot plate and allow the sample to cool completely.
R. After the sample has cooled, remove the snyder column and transfer the sample to a 250 mL acid washed separatory funnel.
S. Extract the sample one time with 50 mL of ethyl ether and discard the ether layer.
T. Acidify the sample with 1:1 sulfuric acid (approximately 10 mL), check the pH with alkacid paper to assure it is acidic. Transfer the sample to a 250 mL separatory funnel.
U. Allow the sample to cool.
V. Extract the sample three times with ethyl ether using 50 mL, 25 mL and 25 mL. Collect the extracts into a clean, acid washed, ether rinsed, dry 125 mL Erlenmeyer flask containing acid washed, anhydrous, baked sodium sulfate (approximately one inch or to the 50 ml mark).
W. Cover the flask with aluminum foil and allow to sit for at least 2 hours.
X. This step is a drying step that removes any water from the ethyl ether extract.

NOTE: If a large batch is being extracted, it is best to get all samples to this point and allow them to dry overnight.

Y. After the sample extract has dried for at least two hours, assemble a KD concentrator by attaching a 10 mL concentrating ampule to a 500 mL KD flask.
Z. Add two to three acid washed boiling chips to the KD flask.
AA. Quantitatively transfer the sample extract to the KD flask.
BB. Rinse the sodium sulfate three times with ethyl ether using 20 mL rinses, and add the rinses to the KD flask.

NOTE: Be sure to break up any 'clumps' of sodium sulfate in the erlenmeyer flask while rinsing.

CC. Attach an ether rinsed three ball macro-Snyder column to the KD apparatus.
DD. Concentrate the extract by evaporating on a hot water bath.

EE. Place the tip of the ampule into the boiling water bath and tap the KD appartus gently until the solvent begins to boil and the balls begin to 'chatter'.

FF. Lower the KD apparatus until the boiling water is at about the level of the 10 mL mark on the concentrating ampule.

GG. Concentrate the sample extract to about 2 mL.

HH. Remove the apparatus from the bath, rinse the snyder column with about 2 mL of methyl-t-butyl ether (MTBE) and allow it to drain and cool.

II. Remove the macro-Snyder column and the KD flask from the ampule, and add approximately 5 mL of MTBE.

JJ. Attach an ether rinsed micro-Snyder column to the ampule.

KK. Pre-elute the micro-Snyder column with MTBE and carefully concentrate the sample to 1 mL on the hot water bath.

LL. Remove the ampule and allow it to cool.

MM. The sample is now ready for derivatization using diazomethane as described on page 105.

IV. Quality control

A. Calibration standards must be prepared by adding 1 mL of the herbicide standard solution to an ether rinsed ampule. Add approximately 5 mL of MTBE and 2 to 3 acid washed boiling chips to the ampule. Concentrate the calibration standard to 1 mL on the hot water bath. The standard is now ready for derivatization using diazomethane.

NOTE: Record the calibration standard in the standard log book, and assign it a calibration standard number.

B. A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 10 grams of washed sand in the same manner as the samples.

C. A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 10 grams of washed sand with 1 mL of the herbicide spiking solution. The standard is then extracted in the same manner as the samples.

D. A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide enough sample to accomodate the SPI and DPS requirements for each group of ten samples. The matrix spikes are prepared by spiking 10 grams of the sample with 1 mL of the herbicide spiking solution, and then extracting in the same manner as the samples.

C. Herbicide Waters - Solid Phase Extraction - P201.4
Reference Method: SW846-3590 (proposed)

THIS PROCEDURE IS NOT TO BE USED!!! NOV. 1,1990 LAJ

1. Theory

The herbicides are extracted from a water sample by passing a quantity of the sample through a cartridge containing a solid inorganic phase coated with a chemically bonded C_{18} organic solid phase. The analytes are eluted from the solid phase with methanol, they are then exchanged into methyl-tert-butyl ether (MTBE), and finally derivatized using gaseous diazomethane gas. The derivatization quantitatively yields esters of the analytes for analysis by gas chromatography.

2. Apparatus

Vacuum manifold/cartridge holder/extractor
70 mL Sample reservoirs for cartridges
Aspirator
10 mL concentrator ampules (acid rinsed)
Micro-Snyder columns (acid rinsed)
Hot water baths
2 dram vials with teflon lined caps
Auto sampler vials
Micro-boiling chips
250 mL graduated cylinder (acid rinsed)

3. Reagents

C_{18} Solid Phase Extraction (SPE) cartridges, 1 mL capacity with 1 gram support
Acetonitrile
Methanol
DI water
Sulfuric acid (1:1)
Acetone
Dilute hydrochloric acid - for acid rinsing
37% aqueous Potassium hydroxide
Methyl-tert-butyl ether

4. Procedure

Attach the sample reservoirs to the SPE (C_{18}) cartridges using the red plastic adapters. Set the cartridges onto the vacuum manifold. Open the flow control valves under the SPE tubes. Condition a column for each sample to be extracted by rinsing, through the reservoirs, with 15 mL of acetonitrile, 15 mL of methanol and finaly 15 mL of acidified DI water. The SPE tubes should be aspirated between each solvent rinse, taking care to avoid carry over of the solvent or complete drying of the columns after the final rinse.

Prepare the samples by measuring out 250 mL aliquots into graduated cylinders which have been acid rinsed with dilute HCL, then DI water and finally acetone. Add 2-3 mL of 1:1 sulfuric acid to the sample, in the graduated cylinder, and verify the pH at less than 2 with alkacid paper. Add 1 mL of acetone to each sample. Cover the samples until ready for extraction. Label the SPE tubes to correspond to the sample numbers. Fill the reservoirs on the SPE tubes with the sample and apply the vacuum to pull the sample through the solid phase.

NOTE: If the sample has solid particulate in it, place a piece of acid washed glass wool in the sample reservoir to retain the solid.

Refill the reservoirs in sequence to prevent drying of the columns. Continue refilling the columns until the entire volume of sample has been aspirated. Rinse the sample containers (graduated cylinders) three times with the acidified DI water, aspirating each rinse.

Once the entire sample has been pulled through, pry the adapters and reservoirs off the columns (may need to use a screwdriver) and set these aside for cleaning. Continue to aspirate the chamber for 20 minutes to remove as much water from the solid phase as possible. It may be necessary to remove water droplets from the inside walls of the columns with 'Kim Wipes'. Disconnect the aspirator and dry the inside of the chamber using paper towels. Insert the collection tube support and place an acid rinsed, labelled, 10 mL concentrating ampule under each column. Replace the chamber cover making certain each column will elute into the appropriate ampule. Add 0.50 mL of methanol to each column and allow the methanol to penetrate the solid phase for 5 minutes. Aspirate until no more bubbles can be seen at the base of the columns. Repeat with an additional 0.50 mL of methanol.

Discard the columns and remove the cover of the manifold chamber. Place an acid rinsed boiling chip in each ampule and attach an acid rinsed micro-Snyder. Boil off the methanol to near dryness on a hot water bath. Allow the ampule to cool and add about 2 mL of MTBE through the top of the micro-Snyder. Remove the microsnyder column from each ampule, rinsing the ground glass joint with MTBE. Quantitatively transfer the extract to a labelled 2 dram vial, rinsing the ampule with a minimum of MTBE. Add 100 uL of a 0.05 mg/L 2-bromobenzoic acid (2-BBA) internal standard solution to each sample, cap and mix. The sample is now ready for derivatization using diazomethane as described on page 105.

5. Quality control

Calibration standards must be prepared by adding 1 mL of the herbicide standard solution to an ether rinsed ampule. Add approximately 5 mL of MTBE and 2 tc 3 acid washed boiling chips to the ampule. Concentrate the calibration standard to 1 mL on the hot water bath. The standard is now ready for derivatization using diazomethane.

NOTE: Record the calibration standard in the standard log book, and assign it a calibration standard number.

A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 250 mL of DI water in the same manner as the samples.

A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 250 mL of DI water with 1 mL of the herbicide spiking solution. The standard is then extracted in the same manner as the samples.

A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide enough sample to accomodate the SPI and DPS requirements for each group of ten samples. The matrix spikes are prepared by spiking 250 mL of the sample with 1 mL of the herbicide spiking solution, and then extracting in the same manner as the samples.

HERBICIDE SOLID PHASE EXTRACTION - Lab bench copy

THIS PROCEDURE IS NOT TO BE USED!!! NOV. 1,1990 LAJ

I. Apparatus
   A. Vacuum manifold/cartridge holder/extractor
   B. 70 mL Sample reservoirs for cartridges
   C. Aspirator
   D. 10 mL concentrator ampules (acid rinsed)
   E. Micro-Snyder columns (acid rinsed)
   F. Hot water baths
   G. 2 dram vials with teflon lined caps
   H. Auto sampler vials
   I. Micro-boiling chips
   J. 250 mL graduated cylinder (acid rinsed)

II. Reagents
   A. C_{18} Solid Phase Extraction (SPE) cartridges, 1 mL capacity with 1 gram support
   B. Acetonitrile
   C. Methanol
   D. DI water
   E. Sulfuric acid (1:1)
   F. Acetone
   G. Dilute hydrochloric acid - for acid rinsing
   H. 37% aqueous Potassium hydroxide
   I. Methyl-tert-butyl ether

IV. Procedure
   A. Attach the sample reservoirs to the SPE (C_{18}) cartridges using the red plastic adapters.
   B. Set the cartridges onto the vacuum manifold.
   C. Open the flow control valves under the SPE tubes.
   D. Condition a column for each sample to be extracted by rinsing, through the reservoirs, with 15 mL of acetonitrile, 15 mL of methanol and finally 15 mL of acidified DI water.

   NOTE: The SPE tubes should be aspirated between each solvent rinse, taking care to avoid carry over of the solvent or complete drying of the columns after the final rinse.

   E. Prepare the samples by measuring out 250 mL aliquots into graduated cylinders which have been acid rinsed with dilute HCL, then DI water and finally acetone.
   F. Add 2-3 mL of 1:1 sulfuric acid to the sample, in the graduated cylinder, and verify the pH at less than 2 with alkacid paper.
   G. Add 1 mL of acetone to each sample.

   NOTE: The samples should be covered until ready for extraction.

   H. Label the SPE tubes to correspond to the sample numbers.
   I. Fill the reservoirs on the SPE tubes with the sample and apply the vacuum to pull the sample through the solid phase.

HERBICIDE SOLID PHASE EXTRACTION - Lab bench copy
THIS PROCEDURE IS NOT TO BE USED!! NOV. 1,1990 LAJ

NOTE: If the sample has solid particulate in it, place a piece of acid washed glass wool in the sample reservoir to retain the solid.

J. Refill the reservoirs in sequence to prevent drying of the columns.

K. Continue refilling the columns until the entire volume of sample has been aspirated.

L. Rinse the sample containers (graduated cylinders) three times with the acidified DI water, aspirating each rinse.

M. Once the entire sample has been pulled through, pry the adapters and reservoirs off the columns (may need to use a screwdriver) and set these aside for cleaning.

N. Continue to aspirate the chamber for 20 minutes to remove as much water from the solid phase as possible.

NOTE: It may be necessary to remove water droplets from the inside walls of the columns with 'Kim Wipes'.

O. Disconnect the aspirator and dry the inside of the chamber using paper towels.

P. Insert the collection tube support and place an acid rinsed, labelled, 10 mL concentrating ampule under each column.

Q. Replace the chamber cover making certain each column will elute into the appropriate ampule.

R. Add 0.50 mL of methanol to each column and allow the methanol to penetrate the solid phase for 5 minutes.

S. Aspirate until no more bubbles can be seen at the base of the columns.

T. Repeat with an additional 0.50 mL of methanol.

U. Discard the columns and remove the cover of the manifold chamber.

V. Place an acid rinsed boiling chip in each ampule and attach an acid rinsed micro-Snyder.

W. Boil off the methanol to near dryness on a hot water bath.

X. Allow the ampule to cool and add about 2 mL of MTBE through the top of the micro-Snyder.

Y. Remove the microsnyder column from each ampule, rinsing the ground glass joint with MTBE.

Z. Quantitatively transfer the extract to a labelled 2 dram vial, rinsing the ampule with a minimum of MTBE.

AA. Add 100 uL of a 0.05 mg/L 2-bromobenzoic acid (2-BBA) internal standard solution to each sample, cap and mix.

BB. The sample is now ready for derivatization using diazomethane as described on page 105.

HERBICIDE SOLID PHASE EXTRACTION - Lab bench copy
THIS PROCEDURE IS NOT TO BE USED!!! NOV. 1,1990 LAJ

IV. Quality control

A. Calibration standards must be prepared by adding 1 mL of the herbicide standard solution to an ether rinsed ampule. Add approximately 5 mL of MTBE and 2 to 3 acid washed boiling chips to the ampule. Concentrate the calibration standard to 1 mL on the hot water bath. The standard is now ready for derivatization using diazomethane.
NOTE: Record the calibration standard in the standard log book, and assign it a calibration standard number.

B. A prep blank (BLA02) should be prepared at the beginning of each prep page, thus providing a blank at a frequency of 10% of the samples. The blank is prepared by extracting 250 mL of DI water in the same manner as the samples.

C. A prep standard (ICV02) should be prepared at the beginning of each prep page, thus providing a standard at a frequency of 10% of the samples. The standard is prepared by spiking 250 mL of DI water with 1 mL of the herbicide spiking solution. The standard is then extracted in the same manner as the samples.

D. A matrix spike (SPI02) and matrix spike duplicate (DPS02) should be prepared at the beginning of each prep page, providing a SPI02 and DPS02 at a frequency of 10% of the samples. The submitter should provide enough sample to accomodate the SPI and DPS requirements for each group of ten samples. The matrix spikes are prepared by spiking 250 mL of the sample with 1 mL of the herbicide spiking solution, and then extracting in the same manner as the samples.

D. Herbicide Diazomethane Derivatization - P201.4
Reference Method: SW846-8150

1. Theory
The herbicide acids must be converted to their methyl esters, using diazomethane as the derivatizing agent, before analysis by gas chromatography. The carboxylic acid group of the herbicides are methylated to obtain better chromatographic separations.

2. Apparatus
Diazomethane generator - bubbler method
Two 20 mL test tubes with two hole rubber stoppers
glass tubing
Nitrogen gas
Ice water bath
2 Dram vials
Autosampler vials

3. Reagents
Ethyl ether
Methyl-tert-butyl ether (MTBE)
Diazald
Carbitol
37% Potassium hydroxide

4. Procedure
Derivatize the samples in the 2 dram vials using the open method (bubbling method) gaseous diazomethane procedure.
NOTE: The calibration standards must be prepared and derivatized at the same time as the samples.
Assemble the diazomethane generator in a fume hood (See figure on page 106). Add a sufficient amount of MTBE to the first test tube to cover the first impinger. Add 1 mL of MTBE, 1 mL of carbitol and approximately 0.5 grams of Diazald to the second test tube. When ready to begin the derivatization add 1.5 mL of potassium hydroxide to the second test tube, seal the tube with a rubber stopper and immediately place the exit tube into the first sample vial.
NOTE: The sample vials should be immersed in an ice water bath while derivatizing.
Apply nitrogen flow at approximately 10 mL/min, to bubble the diazomethane through the extract until the yellow color of diazomethane persists.
NOTE: The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1 to 0.2 grams of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane.

Remove the 2 dram sample vial and loosely cap it with the teflon lined lid. Store the sample vial at room temperature in a hood for 20 minutes.

Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams of silicic acid to the 2 dram sample vial. Allow to stand until the evolution of nitrogen gas has stopped. Quantitatively transfer the sample extract to a 10 mL volumetric flask and bring to volume with hexane. Transfer approximately 1 mL of the sample extract to an autosampler vial for analysis by gas chromatography. Transfer the remainder of the extract to a 2 dram vial for storage.

SAFETY PRECAUTIONS

Diazomethane is a toxic carcinogen which can explode under certain conditions. The following precautions must be followed:

A. Use only a well ventilated hood - do not breath vapors
B. Use a safety screen - or pull the hood sash down as far as possible
C. Do not heat above 90°C - explosion may result
D. Avoid grinding surfaces, ground glass joints, and glass stirrers - explosion may result
E. Store away from alkali metals - explosion may result

NOTE: The diazomethane generation apparatus used produces micromolar amounts of diazomethane to minimize safety hazards.

DIAZOMETHANE DERIVATIZATION - Lab bench copy

I. Apparatus
   A. Diazomethane generator - bubbler method
      Two 20 mL test tubes with two hole rubber stoppers
      glass tubing
      Nitrogen gas
   B. Ice water bath
   C. 2 Dram vials
   D. Autosampler vials

II. Reagents
   A. Ethyl ether
   B. Methyl-tert-butyl ether (MTBE)
   C. Diazald
   D. Carbitol
   E. 27% Potassium hydroxide

III. Procedure
   A. Derivatize the samples in the 2 dram vials using the open method (bubbling method) gaseous diazomethane procedure.
   NOTE: The calibration standards must be prepared and derivatized at the same time as the samples.
   B. Assemble the diazomethane generator in a fume hood (See figure on page 108).
   C. Add a sufficient amount of MTBE to the first test tube to cover the first impinger.
   D. Add 1 mL of MTBE, 1 mL of carbitol and approximately 0.5 grams of Diazald to the second test tube.
   E. When ready to begin the derivatization add 1.5 mL of potassium hydroxide to the second test tube.
   F. Immediately place the exit tube into the first sample vial.
   NOTE: The sample vials should be immersed in an ice water bath while derivatizing.
   G. Apply nitrogen flow at approximately 10 mL/min, to bubble the diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists.
   NOTE: The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1 to 0.2 grams of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane.
   H. Remove the 2 dram sample vial and loosely cap it with the teflon lined lid.
   I. Store the sample vial at room temperature in a hood for 20 minutes.
   J. Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams of silicic acid to the 2 dram sample vial.

DIAZOMETHANE DERIVATIZATION - Lab bench copy

K. Allow to stand until the evolution of nitrogen gas has stopped.
L. Quantitatively transfer the sample extract to a 10 mL volumetric flask and bring to volume with hexane.
M. Transfer approximately 1 mL of the sample extract to an autosampler vial for analysis by gas chromatography.
N. Transfer the remainder of the extract to a 2 dram vial for storage.

SAFETY PRECAUTIONS

Diazomethane is a toxic carcinogen which can explode under certain conditions. The following precautions must be followed:

A. Use only a well ventilated hood - do not breath vapors
B. Use a safety screen - or pull the hood sash down as far as possible
C. Do not heat above 90°C - explosion may result
D. Avoid grinding surfaces, ground glass joints, and glass stirrers - explosion may result
E. Store away from alkali metals - explosion may result

NOTE: The diazomethane generation apparatus used produces micromolar amounts of diazomethane to minimize safety hazards.

III. GC/ECD Analysis Procedure

A. Theory

The methyl esters of the herbicides are single compounds that have a specific retention time under given instrumental conditions. Since these herbicides are identified by the retention time of a single peak, a secondary run on a column of different polarity must be analyzed for confirmation. The herbicides are identified by comparison of the retention time of an eluting sample peak with the retention time of the analytes of interest in the calibration standard. In this analysis, the analytes are only reported if they can be identified on both the primary column and the confirmation column. For most analyses, the DB-5 capillary column is used as the primary column and the DB-608 megabore column is used for confirmation.

Quantitation of the analytes is based on an external calculation using calibration standards that are analyzed in the same analytical sequence as the samples. Using the concentration and the areas of the standard peaks and the area of the sample peaks, the concentration of the analyte in the sample extract can be determined. Adjusting the extract concentration for the sample volume and the final extract volume, the concentration in the sample can be determined.

B. Method - reference SW846-8150

The sample extracts are analyzed using Hewlett-Packard model 5880 or model 5890 gas chromatographs, with an electron capture detector (ECD). A J+W DB-5 capillary column is used for the primary analysis and a J+W DB-608 megabore column is used for the confirmation analysis. Each instrument is configured "dual channel" where two injection ports, two columns and two detectors are in the same instrument. This configuration allows the analysis of the primary and confirmation runs at the same time. An argon/methane mix (P-5) is used as the make-up gas, hydrogen is used as the carrier gas for the DB-5 column and helium is used as the carrier gas for the DB-608 column. The following chromatographic conditions should be used:

1. Temperature program —

	HP-5880	HP-5890
Initial value	130 °C	130 °C
Initial time	3.00 min	3.00 min
Level 1		
Prgm rate	5.00 °C/min	5.00 °C/min
Final value	200 °C	200 °C
Final time	0.00 min	0.00 min
Level 2		
Prgm rate	10.00 °C/min	10.00 °C/min
Final value	250 °C	250 °C
Final time	10.00 min	10.00 min
Level 3		
Prgm rate	25.00 °C/min	28.00 °C/min
Final value	275 °C	278 °C
Final time	0.00 min	0.00 min

2. Injector temperature = 175 °C

3. Detector temperature = 300 °C

4. Attenuation - varies with instrument and detector age

5. Threshold - varies with instrument and detector age

6. Peak width - varies with instrument

7. Gas flows

HP-5880 DB-5 column	
Septum purge	2 to 3 mL/min
Split vent	20 mL/min
Total flow	35 mL/min

HP-5890 DB-5 column	
Total	45 mL/min
Split	18 mL/min
Column	8.00 mL/min
Purge	2 to 3 mL/min

HP-5880 and HP-5890	
Total	45 mL/min
Column	8.8 mL/min

Calibration standards for each analyte are prepared from EPA stock standards. The calibration standards must be derivatized using gaseous diazomethane, at the same time the samples are derivatized. The calibration standard are to contain all analytes of interest.

NOTE: In order to separate the individual analytes, more than one standard may be prepared.

The calibration standard, for the routine analytes, is prepared with the following stock standard solutions:

Analyte	concentration*	Amount used
2,4-D**	2.00 mg/L	2.0 mL
Silvex (2,4,5-TP)**	1.00 mg/L	2.0 mL
2,4,5-T	6.00 mg/L	1.0 mL
2-BBA	1.10 mg/L	0.5 mL

* Standard concentrations may vary slightly

** 2,4-D and Silvex should be in the same standard solution

On each herbicide sequence the following standards should be analyzed:

1. High Herb. - prepare as described in the extraction procedures
2. Medium Herb. - prepare by making a 1:5 dilution of the High
3. Low Herb. - prepare by making a 1:10 dilution of the High
4. Herb RCS - EPA standard (from a different source, usually pre-derivatized)

The calibration standards (High, Med and Low) should be prepared with all analytes of interest, and should be analyzed at the beginning and end of the run. If a sample concentration is outside of the linear range, established by the High, Med and Low standards, the sample must either be diluted or concentrated as needed.

IV. Quality Assurance/Quality Control - analytical

Quality control procedures described by the EPA in Vol. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness and representativeness of its data are known and documented. A start-up test of the instrument in use is done to establish the laboratory's ability to set up and operate the analytical instrumentation and procedures. The purpose is to prove that the compounds of interest can be detected under the parameters set forth and that the analyst can identify the compounds. This test includes a detection limit determination that is performed when a new analysis is first begun and is repeated periodically. Both instrument and method detection limits are determined at this time.

To further assure the representativeness of data produced for the herbicide analyses, internal QA/QC is routinely performed on all types of sample matrices. This QA/QC includes analytical blanks, standards, matrix spikes and matrix spike duplicates.

A. Method (prep) Blanks - BLA02
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run).
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   If the compounds of interest are present in the method blank, any samples with that compound in them that were prepped on the same day must be re-prepped.

   Acceptable limit for the BLA02: below detection limit (BDL) for the specific matrix

B. Method (prep) Standards - ICV02
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run).
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   Results for the Standard are reported as percent recovery using the following formula:

$$\%REC = \frac{\text{Standard Result (concentration)}}{\text{True Value}} \times 100$$

   Acceptable limit for the ICV02 (%R): 60% to 140%

C. Matrix Spike - (SPI02 or MS)
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run).
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

   Results for the Matrix Spike are reported as percent recovery using the following formula:

$$\%REC = \frac{\text{Matrix Spike Result - Sample Result}}{\text{Spike True Value}} \times 100$$

   Acceptable limit for the SPI02 (%R): 60% to 140%

D. Matrix Spike Duplicate - (DPS02 or MSD)
   1. One for each analytical sequence.
   2. One for each prep run (10 samples to a run).
   3. One for each 10 samples in a group of field samples that are of the same matrix.

   Which ever is most frequent.

Results for the Matrix Spike Duplicate are reported as percent recovery using the following formula:

$$\%REC = \frac{\text{Matrix Spike Duplicate - Sample Result}}{\text{Spike True Value}} \times 100$$

Acceptable limit for the DPS02 (%R): 60% to 140%

To show replicability, the relative percent difference (%RPD) is calculated for recoveries of each compound in the spike and spike duplicate, using the following formula:

$$\%RPD = \frac{2|D1 - D2|}{D1 + D2} \times 100$$

Where D1 is the % recovery of the spike and D2 is the % recovery of the spike duplicate.

Acceptable limit for the %RPD: 20%

E. Replicate Control Solution (RCS) - ICV01

One RCS is run during each analytical sequence. The concentration for the RCS is calculated using an average of the beginning and ending High Calibration Standard response factors. The percent recovery of the RCS is reported. This sample is used as an external standard check on the calibration standards. The acceptable limit for the % Recovery is 60 to 140%.

F. Continuing Calibration Verifications - CCV

The CCV is run during each analytical sequence to show consistency in response from the beginning to the end of the run. Both a percent recovery and a percent deviation is calculated. The percent recovery is determined by calculating a concentration for the ending standard using the beginning response factor. The percent recovery is then calculated by comparing the calculated concentration with the true value of the standard. The acceptable limits for the percent recovery is 60 to 140%.

The percent deviation from beginning to end is calculated using the following equation:

$$\%Dev = \frac{\text{Beginning Response - Ending Response}}{\text{Beginning Response}} \times 100$$

The acceptable limit for the percent deviation is 15%.

G. The linearity of the calibration range is calculated using the response factors of the three levels of Herbicide calibration standards at the beginning of the run. The linearity is checked as the percent relative standard deviation (%RSD) of the response factors. The acceptable limit for the %RSD is 10%. If this limit is not met, a calibration curve must be established for the calculations.

I. Data Review

All data generated must be reviewed either by the GC group leader or a designee. The data must be reviewed for completeness and accuracy before being turned in for data entry. The reviewer is responsible for making sure all relevant information has been recorded correctly and that all QA/QC requirements have been met. The reviewer should be sure all sample calculations are complete and are accurately reported. After review of an analytical run, all run sheets should be initialed and dated as well as the run folder.

NOTE: No one can review their own data!

V. Calculations

A. Theory

Using an external calculation with the calibration standards on each analytical run, a sample extract concentration can be determined. Using the extract concentration, the initial weight or volume, the final volume and any dilution factors, the concentration in the sample can be determined.

B. Calculations - Equations

1. Response factors

Response factors are calculated for each standard analyte using the following equation:

$$\text{Resp. Factor} = \frac{\text{concentration of standard}}{\text{area of standard peak}}$$

2. Extract concentration

After identifying the analyte present, the area of the analyte peak is used to calculate the extract concentration using the following equation:

Extr. Conc. = (area of analyte peak) X (Resp. Factor)

3. Sample concentration

Using the extract concentration, the concentration in the sample is determined using the following equation:

$$\text{Sample Conc.} = \frac{(\text{extr.conc.}) \times (\text{final volume})}{\text{Initial weight or volume}}$$

If the sample had to be concentrated or diluted to be within linear range, the sample concentration must be multiplied by any dilution factor and a comment must be added to the run sheet.

VI. Interferences/Troubleshooting

A. Interferences

Organic acids, especially chlorinated acids, cause the most direct interference with the analysis. Phenols, including chlorophenols, may also interfere with this procedure. The alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the analysis. Interferences by phthalate esters can pose a major problem in the analysis. Interferences from phthalate esters can best be minimized by avoiding the use of plastics.

The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

If interferences are such that the analysis can not be completed, a florisil separation may be used to help remove the interferences.

FLORISIL SEPARATION

Place a small plug of glass wool into a 5 mL disposable glass pipet, and measure 1 g of acitivated florisil into the pipet. Apply 5 mL of 5% methanol in MTBE to the florisil. Allow the liquid to just reach the top of the florisil before applying the next rinse, however, do not allow the florisil to go dry. Discard the eluate. Apply 5 mL of the methylated sample to the florisil tube. Collect the eluate in a 10 mL volumetric flask. Add 1 mL of 5% methanol in MTBE to the sample container, rinsing the walls. Transfer the rinse to the florisil column. Collect the eluate in the volumetric flask. Repeat with 1 mL and 3 mL aliqouts of 5% methanol in MTBE, collecting the eluates in the volumetric flask. Dilute the eluate to 10 mL, and transfer 1 mL to an autosampler vial for analysis. Transfer the remaining sample to a 2 dram vial for storage.

NOTE: This is a 1:2 dilution of the origional sample extract. Be certain to label all vials with the dilution factor, and to take the dilution into account during calculations.

B. Troubleshooting

Troubleshooting is most commonly associated with the instrumental analyses. The upkeep of the instruments through routine instrument maintenance should help to reduce the amount of instrument down time. Some things to watch for as an indication of instrument problems are:

1. Inconsistent injections
2. Poor baseline
3. Retention time shifts
4. Peak widening
5. A change in sensitivity

At the first sign of any of these problems the instrument should be checked and steps should be taken to correct the problem.

VII. Safety Precautions

Because the contents of the samples are unknown, they should be treated with caution. Protective equipment such as safety glasses, a lab coat and gloves should be worn when prepping any sample. All liquid/liquid extractions should be done in a fume hood with the sash pulled down as low as possible. The evaporation of the solvents should also be done in a fume hood. There is always a possiblity that the KD apparatus may build up enough pressure to break while concentrating the extract, therefore all glassware should be checked carefully before use for any scratches or nicks that may provide a breakage point.

Diazomethane is a toxic carcinogen which can explode under certain conditions. The following precautions must be followed:

A. Use only a well ventilated hood - do not breath vapors
B. Use a safety screen - or pull the hood sash down as far as possible
C. Do not heat above 90°C - explosion may result
D. Avoid grinding surfaces, ground glass joints, and glass stirrers - explosion may result
E. Store away from alkali metals - explosion may result

NOTE: The diazomethane generation apparatus used produces micromolar amounts of diazomethane to minimize safety hazards.

Ethyl ether is an extremely flammable solvent and is a narcotic. Use only in a fume hood and with extreme caution. The ethyl ether must be free of peroxides.

VIII. Clean up and Disposal

All reusable glassware including separatory funnels, volumetrics, glass funnels, etc. are to be solvent rinsed and the rinse discarded into an appropriate waste container, then washed with hot soapy water, tap water rinsed, acid rinsed, DI water rinsed, acetone rinsed and air dried after use. The glassware should be covered with aluminum foil before storage. Disposable pipets, tounge blades and waste solvents should be placed in the appropriately labeled waste containers for disposal at a later time.

After extraction, sample extracts (2 dram vials) are to be logged into the sample extract cooler and stored. The length of storage time varies according to the submitters' requirements. Normally extracts are kept for at least 3 months before disposal. Extra water samples, that are non-detected for PCBs are disposed of by flushing them down the sink drain with copious amounts of tap water.

WATER DIGESTION FOR ANALYSIS BY FAA OR ICP
(METHOD SW-846 3005A, HL# P130.4)

Submitted by: Ron Byers Title: Trainer, Metals Section

DRAFT

Approval Date

PURPOSE: This document describes a method used to digest water samples for analysis by Flame Atomic Absorption and/or Inductively Coupled Plasma methods. The reference method is SW-846 3005. Adherence to this method will help to ensure accurate and consistent results.

This document replaces SOP # M-10-1.1.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory.

PROCEDURE:

I. PERSONNEL: All metals section personnel directly involved in the digestion of aqueous samples for analysis by FAA or ICP will be trained to follow this method. Training will be conducted by the metals section trainer or a fully qualified designee and documented on appropriate training forms.

II. FACILITIES: This procedure is to be performed in the metals section, in an operating fume hood (#9). All glassware used for this method is stored in the island facing fume hood #9 in the metals prep laboratory.

III. SAFETY: All normal safety apparel must be worn while performing this method. This includes safety glasses, gloves and a lab coat. As an added precaution, a face shield must be worn while adding reagents to samples. All reagents must be added in the fume hood, the sash of the fume hood may be substituted for a face shield if it will provide complete facial protection from splashes and possible explosion.

Additional safety apparel must be worn while adding glassware to or removing glassware from the nitric acid baths. This includes a face shield, heavy rubber apron and acid resistant shoulder length glove.

The fume hood must be operating during all phases of the digestion process. The sash must be lowered to a position which will provide at least 100 CFM of air flow into the fume hood. The sash must be kept at the marked level or lower during normal operation.

IV. EQUIPMENT: Equipment used to perform this procedure includes Metals Section fume hood #9 (or other fume hood if necessary), 150 ml beakers a hot plate, ribbed watch glasses, disposable plastic funnels, 50 ml volumetric flasks and Whatman #541 filter paper.

V. MATERIALS: Nitric acid (HNO3) and hydrochloric acid (HCL) are analytical reagent grade. Deionized water which has been further processed through a Milli-pore filtration system is used for blanks and final dilution of samples. All acids must be stored in designated storage areas or kept in repippettors in fume hood. No acid is to be used past the expiration date on the container. Spiking solutions and laboratory control samples are prepared by the trainer or a fully trained designee. Spiking solutions and laboratory control samples are stored in designated containers. No spiking solution or laboratory control sample is to be used after the expiration date on the container(s).

VI. SAMPLE REQUIREMENTS: Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers to glass containers of various sizes. All samples must be preserved with nitric acid to pH <2.0. Sample volume must be enough to support this digestion and all other analyses required. Holding time for samples may be from 3 to 6 months with sample disposal at 3 months from date of report unless a longer period is preferred by the client. Check with the Metals Group Prep Supervisor before disposing of any samples.

VII. DIGESTION PROCEDURE: All prep sets will consist of 10 or fewer samples. EACH SET MUST CONTAIN THE FOLLOWING QA/QC SAMPLES; BLA02, LCS, SPI02 AND DUP02 OR DPS02. Label each beaker with the appropriate sample number,sample volume being digested and the date of digestion. Transfer a 50 ml aliquot of well mixed sample to a labelled beaker. Add 1.0 ml of HNO3 and 2.5 ml of HCL, cover the beaker with a watch glass and place beaker on a hot plate. Heat at 95°C and reflux sample until volume is reduced to 10-15 ml.

While samples are refluxing fill-in sample prep information on BLUE LABELS. Include all pertinent information; sample number, QC type, initial and final volumes, R & Q #s from prep bench sheet, date of digestion and analyst initials. Attach labels to 120 ml plastic bottles. Label the lid of each container with sample number, QC type (if applicable) and date.

When sample volume has reached desired volume, remove the beaker from the hot plate and allow to cool. Place a folded Whatman 541 filter paper in a plastic funnel, filter and bring to volume in a 50 ml volumetric flask. Transfer samples to respective containers, place containers in a plastic bin along with a copy of the prep bench sheet. Label a BLUE piece of file card with run #, sample numbers, date and analyst initials. Place file card in slot on front of plastic sample bin and deliver samples in the bin to the FAA/ICP lab.

Quality Control: All samples are to prepared in the exact same manner, following Standard Operating Procedure. Every effort must be made to ensure a homogeneous representative subsample is used for each sample within the set to provide accurate and reproducible results. All requirements of Heritage Laboratories Comp. QAP must be met.

If any deviation from SOP is indicated by sample matrix or safety concerns, contact the Metals Group Leader or Prep supervisor before beginning digestion. All matrix spike solutions must be added prior to digestion. This includes Sn and Sb spikes for LCS samples when required. All Laboratory Control Samples ,Duplicate samples and Blanks must be completely digested at the same time as all other samples within the set. All samples within a set must be digested on the same hot plate. Care must be taken to document every sample digestion procedure accurately on the bench sheet. Document any abnormalities in reaction, sample matrix or physical properties observed during digestion or filtration. Carefully select and record quality control samples (some clients require QC samples from each set of samples they submit) on bench sheet. Record all volumes and all lot numbers of spike solutions and standards.

Do not forget the importance of accuracy in documentation of sample numbers, sample weights and volumes, dates, analyst identification and methodology practiced.

DOCUMENTATION: All samples must be documented on a "stepped" prep bench sheet. These bench sheets are prenumbered by the Data Entry staff and contain all Run numbers and Q numbers. Sample numbers, QC sample numbers, initial and final volumes, due dates, elements of interest and analytical codes are recorded on the main body of the bench sheet.

Prep code, date, analyst initials and employee number are recorded in the upper left corner of the sheet. All reagents and prep solutions used are recorded in lower right corner of the sheet. Include reagent batch numbers. Also include the reference number and volume used for all spike solutions and laboratory control samples.

This procedure was developed specifically for use by HERITAGE LABORATORIES, INC. and may not be applicable for other organizations.

AQUEOUS SAMPLE PREPARATION FOR ANALYSIS BY FAA OR ICP (SW-846 3010A, HL# P130.5, P130.8)

Submitted by: Ron Byers Title: Trainer, Metals Section

DRAFT

Approval Date

PURPOSE: This document describes a procedure used to digest aqueous samples and leachate (TCLP) extract samples for analysis by Flame Atomic Absorption and/or Inductively Coupled Plasma techniques. The reference method is SW-846-3010A. This document replaces SOP # AM 201.0.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory. The reference method is SW-846 3010A.

PROCEDURE:

I. PERSONNEL: All metals section personnel involved in digesting aqueous samples and/or leachate samples for analysis by FAA and/or ICP will be trained to adhere to this method. Training will be conducted by the metals section trainer or a fully qualified designee and documented on appropriate training forms.

II. FACILITIES: This procedure is to be performed in the metals prep laboratory, in an operating fume hood. The aqueous samples are normally digested in fume hood #9 and leachate samples are digested in fume hood #8. The glassware used for each type of sample is stored in the island directly opposite the respective fume hoods.

III. SAFETY: All normal safety apparel must be worn while performing this procedure. This includes safety glasses, gloves and a lab coat. As an added precaution, a face shield must be worn while adding reagents to samples. All reagents must be added in the fume hood. Additional safety apparel must be worn while adding glassware to or removing glassware from the nitric acid baths. This includes a face shield, acid resistant shoulder length glove and a heavy rubber apron. The fume hood must be operating during all phases of the digestion process. The sash must be lowered to a position which will provide at least 100 CFM of air flow into the fume hood. The sash must kept at the marked level or lower during normal operation.

IV. **EQUIPMENT:** Equipment used to perform this procedure includes appropriate fume hood (see Section II), hot plates, beakers, volumetric flasks, graduated cylinders, watch glasses, disposable plastic funnels and Whatman #541 filter paper.

V. **MATERIALS:** Nitric acid (HNO_3) and hydrochloric acid (HCL) used in this procedure are analytical reagent grade. Deionized water which has been further processed through a Milli-pore filtration system is used for blanks and final dilutions of samples. All acids must be stored in designated storage areas or kept in repippettors in the fume hood. No acid is to be used past the expiration date on the container.

Spiking solutions and laboratory control samples are prepared by the trainer or a fully trained designee. Spiking solutions and laboratory control samples are stored in designated containers. No spiking solution or laboratory control sample is to be used after the expiration date on the container(s).

VI. **SAMPLE REQUIREMENTS:** Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers. Glass containers of various sizes may also be used.

All samples MUST be preserved with nitric acid to a pH <2.0, this is normally done in the field. Sample volume must be sufficient to support this digestion and all other metals analyses required.

Holding time for samples range from 3 to 6 months, sample disposal at 3 months from the date of the final report unless a longer period is specified by the client. Check with the metals section prep supervisor before disposing of any samples.

VII. **DIGESTION PROCEDURE:** All prep sets will consist of 10 or fewer samples. Aqueous sample sets must contain the following QA/QC samples; BLA02, LCS, SPI02 and DUP02 or DPS02. Leachate sample sets must contain BLA02, LCS, DUP02 and any TCLP matrix bias spikes required by the client. Label each beaker with the appropriate sample number, sample volume being digested and the date of the digestion.

Transfer a 50 ml aliquot of well mixed sample to a beaker (100 ml for leachate samples). Add 1.5 ml of concentrated HNO_3 (3.0 ml for leachate samples). Cover beaker with a watch glass and place beaker on the hot plate. Heat samples at 95°C and allow to reflux until volume is reduced to 15 ml (30 ml for leachate samples). DO NOT ALLOW SAMPLE TO BOIL OR EVAPORATE TO DRYNESS. Cool the beaker and add an additional 1.5 ml of HNO_3 Allow sample to reflux until digestion is complete, this is indicated by a light color of the solution or no change of color after continued refluxing. Add more HNO_3 (1 ml increments) if needed to complete digestion.

Cool the sample and add 2.5 ml of concentrated HCL. Return beaker to hot plate and reflux gently for 15 minutes to dissolve any precipitates present. Remove the beaker from the hot plate and allow to cool. If no solid material is present in the solution, filtering may not be necessary. However, if any sample within a set requires filtration, all samples in that set MUST be filtered. Place a plastic funnel in a volumetric flask, place a Whatman 541 filter in the funnel (if filtration is necessary) and rinse the watch glass into the funnel. Rinse the beaker walls with a small amount of deionized water and pour the solution into the funnel/filter. Rinse the walls of the beaker three additional times to ensure recovery of all analyte. Bring sample solution to required final volume.

Fill-in sample prep information on BLUE LABELS (GREEN for LEACHATES). Include sample #, QC type, initial and final volumes, R & Q numbers from bench sheet, date of digestion and analyst initials. Attach labels to 120 ml plastic bottles. Label the lid of each bottle with sample number, QC type (if applicable) and date of digestion. Attach labels to 120 ml plastic bottles and label each lid with sample number, QC type (if applicable) and date of digestion.

Quality Control: All samples are to prepared in the exact same manner, following Standard Operating Procedure. Every effort must be made to ensure a homogeneous representative subsample is used for each sample within the set to provide accurate and reproducible results. All requirements of Heritage Laboratories Comp. QAP must be met.

If any deviation from SOP is indicated by sample matrix or safety concerns, contact the Metals Group Leader or Prep supervisor before beginning digestion. All matrix spike solutions must be added prior to digestion. This includes Sn and Sb spikes for LCS samples when required.

All Laboratory Control Samples ,Duplicate samples and Blanks must be completely digested at the same time as all other samples within the set. All samples within a set must be digested on the same hot plate. Care must be taken to document every sample digestion procedure accurately on the bench sheet. Document any abnormalities in reaction, sample matrix or physical properties observed during digestion or filtration.

Carefully select and record quality control samples (some clients require QC samples from each set of samples they submit) on bench sheet. Record all volumes and all lot numbers of spike solutions and standards.

Do not forget the importance of accuracy in documentation of sample numbers, sample weights and volumes, dates, analyst identification and methodology practiced.

DOCUMENTATION: All samples must be documented on a "stepped" prep bench sheet. These bench sheets are prenumbered by the Data Entry staff and contain all Run numbers and QC numbers. Sample numbers, QC sample numbers, initial and final volumes, due date(s), elements of interest and analytical codes are recorded on the bench sheet.

Prep code, date, analyst initials and employee number are recorded in the upper left hand corner of the bench sheet. All reagents and prep solutions used are recorded in the lower right hand corner of the bench sheet. Include reagent lot numbers. Also include the reference number and volume used for all reagents, spike solutions and laboratory control samples. Original bench sheets are given to the Metals Prep Supervisor. A copy of the bench sheet must accompany each set of samples in the plastic bin. Another copy of the bench sheet is placed in a logbook to be kept at the bench for easy reference.

This procedure was developed specifically for use by HERITAGE LABORATORIES,INC. and may not be applicable for other organization.

AQUEOUS SAMPLE PREPARATION FOR ANALYSIS BY GFAA
(SW846 3020A - HLI # P130.6, P130.9)

Submitted by: Ron Byers Title: Trainer, Metals Section

DRAFT

Approval Date

PURPOSE: This document describes the procedure used to digest aqueous samples and leachate (TCLP) extract samples for analysis by Graphite Furnace Atomic Absorption techniques. This document replaces SOP # AM 202.1.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory. The reference method is SW-846 3020A.

PROCEDURE:

I. **PERSONNEL:** All Metals Section personnel involved in digesting aqueous samples and/or leachate samples for analysis by GFAA will be trained to adhere to this method. Training will be conducted by the Metals Section Trainer or by a fully qualified designee. Training will be documented on the appropriate training forms.

II. **FACILITIES:** This procedure is to be performed in the Metals Prep Laboratory, in an operating fume hood. The aqueous samples are digested in the Graphite Furnace Waters Prep Room. All glassware used for aqueous sample digestion is stored in this room.

Leachate sample digestion is done in fume hood #8 the Metals Prep Laboratory. All glassware for leachate digestion is stored in the island directly opposite fume hood #8.

III. **SAFETY:** All normal safety apparel must be worn while performing this procedure. This includes safety glasses, gloves and a lab coat. As an added precaution, a face shield must be worn while adding reagents samples. All reagents must be added in the fume hood.

Additional safety apparel must be worn while adding glassware to or removing glassware from the nitric acid baths. This includes a face shield, acid resistant shoulder length glove and a heavy rubber apron.

The fume hood must be operating during all phases of the digestion process. The sash must be lowered to a position which will provide at least 100 CFM of air flow into the fume hood. The sash must kept at the marked level or lower during normal operation.

IV. **EQUIPMENT:** Equipment used to perform this procedure includes appropriate fume hood (see Section II), hot plates, beakers, volumetric flasks, watch glasses, disposable plastic funnels and Whatman #541 filter paper.

V. **Materials:** Nitric acid (HNO_3) used in this procedure is analytical reagent grade. Deionized water which has been further processed through a Millipore filtration system is used for blanks and final dilutions of samples. All acids must be stored in designated storage areas or kept in repippettors in the fume hood. No acid is to be used past the expiration date on the container.

Spiking solutions and laboratory control samples are prepared by the trainer or a fully trained designee. Spiking solutions and laboratory control samples are stored in designated containers. No spiking solution or laboratory control sample is to used after the expiration date on the container(s).

VI. **SAMPLE REQUIREMENTS:** Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers. Glass containers of various sizes may also be used. All samples MUST be preserved with nitric acid to a pH <2.0, this is normally done in the field. Sample volume must be sufficient to support this digestion and all other metals analyses required. Holding time for samples range from 3 to 6 months, sample disposal at 3 months from the date of the final report unless a longer period is specified by the client. Check with the metals section prep supervisor before disposing of any samples.

VII. **DIGESTION PROCEDURE:** All prep sets will consist of 10 or fewer samples. Aqueous sample sets must contain the following QA/QC samples; BLA02, LCS, SPI02 and DUP02 or DPS02. Leachate sample sets must contain BLA02, LCS, DUP02 and any TCLP matrix bias spikes required by the client. Label each beaker with the appropriate sample number, sample volume being digested and the date of the digestion.

Transfer a 50 ml aliquot of well mixed sample to a beaker. Add 1.5 ml of concentrated HNO_3. Cover beaker with a watch glass and place beaker on the hot plate. Heat samples at 95°C and allow to reflux until volume is reduced to 15 ml (30 ml for leachate samples). **DO NOT ALLOW SAMPLE TO BOIL OR EVAPORATE TO DRYNESS.**

Cool the beaker and add an additional 1.5 ml of HNO_3. Allow sample to reflux until digestion is complete, this is indicated by a light color of the solution or no change of color after continued refluxing. Add more HNO_3 (1 ml increments) if needed to complete digestion. Cool the sample and add 10 ml of deionized water (Milli-Q).

Return beaker to hot plate and reflux gently for 15 minutes to dissolve any precipitates present. Remove the beaker from the hot plate and allow to cool. If no solid material is present in the solution, filtering may not be necessary. However, if any sample within a set requires filtration, all samples in that set MUST be filtered. Place a plastic funnel in a volumetric flask, place a Whatman 541 filter in the funnel (if filtration is necessary) and rinse the watch glass into the funnel. Rinse the beaker walls with a small amount of deionized water and pour the solution into the funnel/filter. Rinse the walls of the beaker three additional times to ensure recovery of all analyte. Dilute sample solution to required final volume with Milli-Q H_2O. Fill-in sample prep information on BLUE LABELS (GREEN for LEACHATES).

Include sample numbers, QC type, initial and final volumes, R & Q numbers from bench sheet, date of digestion and analyst initials. Attach labels to 120 ml plastic bottles. Label the lid of each bottle with sample number, QC type (if applicable) and date of digestion.

DOCUMENTATION: All samples must be documented on a "stepped" prep bench sheet. These bench sheets are prenumbered by the Data Entry staff and contain all Run numbers and QC numbers. Sample numbers, QC sample numbers, initial and final volumes, due date(s), elements of interest and analytical codes are recorded on the bench sheet.

Prep code, date, analyst initials and employee number are recorded in the upper left hand corner of the bench sheet.

All reagents and prep solutions used are recorded in the lower right hand corner of the bench sheet. Include reagent lot numbers. Also include the reference number and volume used for all reagents, spike solutions and laboratory control samples.

Original bench sheets are given to the Metals Prep Supervisor. A copy of the bench sheet must accompany each set of samples in the plastic bin. Another copy of the bench sheet is placed in a logbook to be kept at the bench for easy reference.

This procedure was developed specifically for use by HERITAGE LABORATORIES, INC. and may not be applicable for other organizations.

ACID DIGESTION OF OILS FOR ANALYSIS BY FAA, GFAA & ICP (SW-846 3030 MODIFIED, HLI# P130.0)

Submitted by: Ron Byers

Title: Trainer, Metals Section

THIS IS AN EXACT COPY OF THE ORIGINAL DOCUMENT

Gary P. Klingler
Approval

5-21-93
Date

PURPOSE: This document describes the procedure used to digest oil sample or samples with an organic phase for analysis by Flame Atomic Absorption, Graphite Furnace Atomic Absorption and/or Inductively Coupled Plasma (Emission) techniques. This procedure is also used to digest oil/organic phases of TCLP or other leachate samples. This SOP replaces M-10-4.1.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory. The reference method is SW-846 3030. This a modified version of the SW-846 3030 method.

PROCEDURE:

I. **PERSONNEL:** All Metals Section personnel involved in digesting oil samples and/or leachate samples with an oil/organic phase for analysis by FAA,ICP and/or GFAA will be trained to adhere to this method.

Training will be conducted by the Metals Section Trainer or by a fully qualified designee. Training will be documented on the appropriate training forms.

II. **FACILITIES:** This procedure is to be performed in the Metals Prep Laboratory, in an operating fume hood. All oil digestions are performed in fume hood #6 or in fume hood #5 if additional space is required.

III. **SAFETY:** All normal safety apparel must be worn while performing this procedure. This includes safety glasses, gloves and a lab coat. As an added precaution, a face shield must be worn while adding reagents samples. All reagents must be added in the fume hood.

Additional safety apparel must be worn while adding glassware to or removing glassware from the nitric acid baths. This includes a face shield, acid resistant shoulder length glove and a heavy rubber apron.

The fume hood must be operating during all phases of the digestion process. The sash must be lowered to a position which will provide at least 100 CFM of air flow

into the fume hood. The sash must kept at the marked level or lower during normal operation.
Heat resistant gloves and finger covers should be used when handling the hot oil digestion flasks.

IV. **EQUIPMENT:** Equipment used to perform this procedure includes appropriate fume hood (see Section II), hot plates, Erlenmeyer flasks, volumetric flasks, watch glasses, disposable plastic funnels, glass boiling beads and Whatman #541 filter paper.

An analytical balance (Allied Model #7240DA) which is accurate to 0.01g is used to weigh subsamples for digestion.

V. **MATERIALS:** Nitric acid ($HN0_3$) and hydrogen peroxide (H_2O_2) used in this procedure are analytical reagent grade. Deionized water which has been further processed through a Milli-pore filtration system is used for blanks and final dilutions of samples. All acids must be stored in designated storage areas or kept in repippettors in the fume hood. No acid is to be used past the expiration date on the container.

Spiking solutions and laboratory control samples are prepared by the trainer or a fully trained designee. Spiking solutions and laboratory control samples are stored in designated containers. No spiking solution or laboratory control sample is to used after the expiration date on the container(s).

VI. **SAMPLE REQUIREMENTS:** Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers. Glass containers of various sizes may also be used. Sample volume must be sufficient to support this digestion and all other metals analyses required.

Holding time for samples range from 3 to 6 months, sample disposal at 3 months from the date of the final report unless a longer period is specified by the client. Check with the metals section pre · supervisor before disposing of any samples.

VII. **DIGESTION PROCEDURE:** Label an Erlenmeyer flask (500 ml cap.) with appropriate sample number, initial sample weight, date of digestion and analyst initials. Place the flask on the balance weigh a 2g representative subsample (4g for a TCLP sample or matrix spike) and add several glass boiling beads to the flask. **CAREFULLY** add 25 ml of concentrated HNO_3; place the flask on the hot plate and cover with a ribbed watch glass. Swirl the flask to mix contents and aid in complete digestion of the sample.

Heat the sample at a medium high setting and boil until dense orange fumes appear. Continue heating sample and add HNO_3 in 1 ml increments until oxidation is

complete and orange fumes are no longer being produced. At this point the sample solution should have a light orange or "straw" color.

Cool the flask and carefully add 1ml of H_2O_2 immediately followed by 1 ml of HNO_3 and heat until white fumes appear. Continue adding H_2O_2 and HNO_3 in 1 ml increments until solution is colorless. Some sample solution may not become totally colorless, add reagents until white fumes are no longer being produced and no change in color is noted after 5-6 additions of the reagents.
Cool the flask and rinse the watch glass and walls of the flask with 5-10 ml of deionized water. Swirl flask to mix contents and heat for 15 minutes. White fumes may reappear. Cool the contents to room temperature before filtration.

Place a Whatman #541 filter paper in a plastic funnel atop a 100 ml volumetric flask. Filter the cooled sample, rinse walls of the flask several times (5-6 minimum) with deionized water to remove sample solution from flask.

Bring sample to volume with deionized water and transfer to a labelled 120 ml plastic bottle or split sample solution into separate aliquots for instrument analyses as needed.

VIII. QUALITY CONTROL: All samples are to prepared in the exact same manner, following Standard Operating Procedure. Every effort must be made to ensure a homogeneous representative subsample is used for each sample within the set to provide accurate and reproducible results. If any deviation from SOP is indicated by sample matrix or safety concerns, contact the Metals Group Leader or Prep supervisor before beginning digestion. All matrix spike solutions must be added prior to digestion. This includes Sn and Sb spikes for LCS samples when required. All Laboratory Control Samples, Duplicate Samples and Blanks must be completely digested at the same time as all other samples within the set. All samples within a set must be digested on the same hot plate whenever possible.

Care must be taken to document every sample digestion procedure accurately on the bench sheet. Document any abnormalities in reaction, sample matrix or physical properties observed during digestion or filtration. Carefully select and record quality control samples (some clients require QC samples from each set of samples they submit) on bench sheet. Record all volumes and all lot numbers of spike solutions and standards.

Do not forget the importance of accuracy in documentation of sample numbers, sample weights and volumes, dates, analyst identification and methodology practiced.

DOCUMENTATION: All samples must be documented on a "stepped" prep bench sheet. These bench sheets are prenumbered by the Data Entry staff and contain all Run numbers and QC numbers. Sample numbers, QC sample numbers, initial and

final volumes, due date(s), elements of interest and analytical codes are recorded on the bench sheet.

A single oil digestion is often split for 2 or 3 analyses by different instruments. A special "stepped" bench sheet is used to record all LCS, Blank, Duplicate samples and Matrix Spike samples needed for each type of analysis. Each split or separate QC sample is assigned a "Q" number to facilitate data entry and QC data retrieval. Prep code, date, analyst initials and employee number are recorded in the upper left hand corner of the bench sheet (or cover sheet).

All reagents and prep solutions used are recorded in the lower right hand corner of the bench sheet. Include reagent lot numbers. Also include the reference number and volume used for all reagents, spike solutions and laboratory control samples. Original bench sheets are given to the Metals Prep Supervisor. A copy of the bench sheet must accompany each set of samples in the plastic bin. Another copy of the bench sheet is placed in a logbook to be kept at the bench for easy reference.

This procedure was developed specifically for use by HERITAGE LABORATORIES, INC. and may not be applicable for other organizations.

SOLID SAMPLE DIGESTION FOR ANALYSIS BY FAA, GFAA AND ICP (SW846 3050A, HLI# P129.7, P130.7)

DRAFT

Submitted by: Ron Byers Title: Trainer, Metals Section

Approval Date

PURPOSE: This document describes the method used to digest soil, sediment and sludge samples for analysis by Flame and Graphite Furnace Atomic Absorption techniques and Inductively Coupled Plasma (Emission). This document replaces SOP # 203.0.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory. The reference method is SW846 3050A.

PROCEDURE:

I. PERSONNEL: All Metals Section personnel involved in digesting soil, solid and/or sludge samples for analysis by GFAA, FAA and ICP will be trained to adhere to this method. Training will be conducted by the Metals Section Trainer or by a fully qualified designee. Training will be documented on the appropriate training forms.

II. FACILITIES: This procedure is to be performed in the Metals Prep Laboratory, in an operating fume hood. The fume hood normally used for solid digestion is fume hood #5, with fume hood #6 used to handle overflow samples.

An analytical balance is used to weigh subsamples. This balance must be accurate to 0.01g and is to be checked on a daily basis with an "S" class by the analyst.

III. SAFETY: All normal safety apparel must be worn while performing this procedure. This includes safety glasses, gloves and a lab coat. As an added precaution, a face shield must be worn while adding reagents to samples. All reagents must be added in the fume hood.

Additional safety apparel must be worn while adding glassware to or removing glassware from the nitric acid baths. This includes a face shield, acid resistant shoulder length glove and a heavy rubber apron.

The fume hood must be operating during all phases of the digestion process. The sash must be lowered to a position which will provide at least 100 CFM of air flow into the fume hood. The sash must kept at the marked level or lower during normal operation.

IV. **EQUIPMENT:** Equipment used to perform this procedure includes Beakers (100 ml), watch glasses, plastic funnels and volumetric flasks (50 ml and 100 ml). An analytical balance is used to weigh subsamples (see Section II). Hot plates are used to reflux samples.

V. **MATERIALS:** Nitric acid (HNO_3) and hydrochloric acid (HCL) used in this procedure must be analytical reagent grade. Deionized water which has been further processed through a Milli-pore filtration system is used for blanks and final dilutions of samples. All acids must be stored in designated storage areas or kept in repippettors in the fume hood. No acid is to be used past the expiration date on the container.

Spiking solutions and laboratory control samples are prepared by the trainer or a fully trained designee. Spiking solutions and laboratory control samples are stored in designated containers. No spiking solution or laboratory control sample is to be used after the expiration date on the container(s).

VI. **SAMPLE REQUIREMENTS:** Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers. Glass containers of various sizes may also be used. Sample disposal is to be done by personnel trained in proper disposal procedures.

VII. **DIGESTION PROCEDURE:** Mix all samples thoroughly to ensure homogeneity of samples. Transfer a 1.00g subsample (2.00g for FAA) to a 100 ml beaker. CAREFULLY add 10 ml of 1+1 HNO_3, cover with a watch glass, place the beaker on a hot plate and heat at 95°C for 15 minutes. Do not allow sample solution to boil.

Cool the beaker and add 5 ml of concentrated HNO_3 and reflux for 30 minutes. Cool the beaker, add an additional 5 ml of concentrated HNO_3 and reflux until sample volume is reduced to approximately 5 ml.

Cool the beaker, add 2 ml of deionized H_2O and CAREFULLY add 3 ml of 30% H_2O_2. Return the beaker to the hot plate to initiate peroxide reaction. Heat until effervescence subsides and add H_2O_2 in 1 ml aliquots until effervescence is minimal or sample appearance is no longer changing. Do not add more than 10 ml of H_2O_2. For samples requiring analysis by GFAA, add 10 ml of deionized H_2O and heat until volume is reduced to approximately 5 ml.

For samples requiring analysis by FAA and/or ICP, add 5 ml of concentrated HCL and 10 ml of deionized H_2O and reflux for 15 minutes. Filter sample through a Whatman #541 filter and dilute to volume in a 100 ml volumetric flask.

QUALITY CONTROL: All samples are to prepared in the exact same manner, following Standard Operating Procedure. Every effort must be made to ensure a homogeneous representative subsample is used for each sample within the set to provide accurate and reproducible results. All requirements of Heritage Laboratories Comp. QAP must be met.

If any deviation from SOP is indicated by sample matrix or safety concerns, contact the Metals Group Leader or Prep supervisor before beginning digestion.

All matrix spike solutions must be added prior to digestion. This includes Sn and Sb spikes for LCS samples when required.

All Laboratory Control Samples, Duplicate samples and Blanks must be completely digested at the same time as all other samples within the set. All samples within a set must be digested on the same hot plate. Care must be taken to document every sample digestion procedure accurately on the bench sheet. Document any abnormalities in reaction, sample matrix or physical properties observed during digestion or filtration. Carefully select and record quality control samples (some clients require QC samples from each set of samples they submit) on bench sheet. Record all volumes and all lot numbers of spike solutions and standards. Do not forget the importance of accuracy in documentation of sample numbers, sample weights and volumes, dates, analyst identification and methodology practiced.

DOCUMENTATION: All samples must be documented on a "stepped" prep bench sheet. These bench sheets are prenumbered by the Data Entry staff and contain all Run numbers and Q numbers. Sample numbers, QC sample numbers, initial and final volumes, due date(s), elements of interest and analytical codes are recorded on the bench sheet.

Prep code, date, analyst initials and employee number are recorded in the upper left hand corner of the bench sheet. All reagents and prep solutions used are recorded in the lower right hand corner of the bench sheet. Include reagent lot numbers. Also include the reference number and volume used for all reagents, spike solutions and laboratory control samples.

Original bench sheets are given to the Metals Prep Supervisor. A copy of the bench sheet must accompany each set of samples in the plastic bin. Another copy of the bench sheet is placed in a logbook to be kept at the bench for easy reference.

This procedure was developed specifically for use by HERITAGE LABORATORIES INC. and may not be applicable for other organizations.

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M-2
GFAA ANALYSIS

THIS IS AN EXACT COPY OF
THE ORIGINAL DOCUMENT
BY _____ DATE _____

I. THEORY

Graphite furnace atomic absorption is an analytical method commonly used for samples with low level concentrations of metals. Concentrations are measured in ~~mg~~ µg/l or parts per billion.

Normal elements of interest include As, Se, Pb, Cd, Tl, Ag, and Sb.

This method utilizes a light source (hollow cathode or electrodeless discharge lamp) which emits a sharp line at a specific wavelength. The light beam is directed through a tube of pyrolytically coated graphite. The tube and graphite platform inside are heated electrothermaly in the furnace.

After injection of sample takes place the furnace heats the solution in a series of steps, typically:

1. Dry at 130°C for 30 seconds.
2. Dry at 400°C for 5 seconds.
3. Char or Ash at 800°-1300°C for 20 seconds.
4. Cool at 20°C for 10 seconds.
5. Atomize at 1700°-2300°C for 5 seconds.
6. Purge at 2500°C for 5 seconds.

Argon gas is used to purge the tube during all steps but the atomization step.

As the sample is atomized, excited atoms will absorb light from the beam. Light not absorbed passes through the tube and is measured by a detector.

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The Zeeman Background Correction Method is used to correct for non-specific absorption.

A magnetic field is applied around the tube, perpendicular to the light path. The magnetic field is modulated and polarizes the background signal. The background absorbance is subtracted from the total absorbance to obtain the correct reading.

Absorbance reading are then converted to concentration using a curve generated by reading a 4 part series of standards.

II. METHOD

Switch power on to the instrument and all ancillary equipment. Turn on gas flow and warm up a lamp for the desired element.

Select elements of interest using computer and enter all necessary information. This includes type of analysis, number of auto sampler cups, location of standards and other QC samples.

The tube and platform should be checked for wear and replaced if needed.

Auto sampler alignment and delivery should also be checked to ensure good results.

Place samples in auto sampler cups. Each sample will require an analytical spike ($\simeq$ 2 X D.L.).

On PE3030 fill cups with 900μl of sample in two separate cups. Add 100μl of matrix modifier to the first cup and 100μl of spiked modifier to the second cup.

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On PE100 fill cups directly from samples. Modifier and spike solutions will be added automatically by the instrument.

Enter sample numbers and auto-sampler locations into computer (10/weight parameter section).

A set of calibration standards is run first to establish a curve. A typical set includes 5ppb, 10ppb, 20ppb, and 40ppb standards.

Linearity ≥ .9950 is needed before samples may be analyzed.

Record linearity, y intercept, lamp energy and characteristic concentration values in log book for instrument.

Before running any samples analyze a blank (BLA01) and an initial calibration verification standard (ICV01). Acceptance criteria for ICV01 is 85% - 115% of trune value, except for CLP and other special analyses which require 90% - 110% recovery. Also run a critical detection limit standard at this time. CDL should be equal in concentration to 2 x instrument detection limit.

ICV01 must be from an approved EPA source. Continuing calibration verification standards must also be run after each set of 10 samples. CCV standards may be from a different source, but normally the same source (EPA) is used. CCV must also meet same acceptance criteria as ICV01.

A blank (BLA02), laboratory control sample (LCS), duplicate (DUP02) and spiked duplicate (SP102) must be prepped and analyzed with each set of 10 samples.

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Clean water samples not requiring acid digestion may be analyzed with a BLA01, ICV01, and CDL01 to begin run. Select a sample from each set of 10 for duplicate analysis (DUP01).

Analytical spike recovery must be 85 to 115% of true value of spike. Spike recovery for blanks and other samples below detection limit must be ≥ 40% and absorbance reading must have absolute values no more than that of detection limit calibration standard.

Some samples may require 3 pt standard additions. Run each sample, followed by aliquots spiked with 3 standards of known concentration.

At the end of each run always analyze a BLA01, CCV, and CDL01 to verify instrument stability.

Label printout with initials, date, element, and run number from cover sheet. Complete all paperwork, remembering to include sample type. Prep and/or dilution factors, detection limits and all other pertinent information. Multiply raw concentrations by prep factor (i.e. 2g/50 = Factor of 25) and any dilutions made at instrument (i.e. 1:10 dilution = Factor of 10).

Turn completed paperwork in to supervisor for review.

SOP Correction FORM

SOP Number: IM-10-12.0

SOP Title: ICP/MS Analysis

Page #: 3 of 4

Requested by : Curtis Bopp Date: 12/3/92

Correction: Recovery criteria for ICV01 is 90 to 110% of true value.

Reason (if applicable):

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager Signature: [signature] Date: 12-3-92

100892

SOP Correction FORM

SOP Number: [illegible]

SOP Title: SFAA analysis

Page #: 4 of 4

Requested by : [illegible] Date: 12/3/92

Correction: Determinations of when to analyze samples by 3 point method or standard additions are made using CLP logic.

Reason (if applicable): _____

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: [illegible] Date: 2-3-92

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HERITAGE LABORATORIES, Inc.

SOP Correction FORM

SOP Number: M-10-12.0

SOP Title: GFAA Analysis

Page #: 1

Requested by : Dave C Date: 1-6-94

Correction: Add SW 846 7061 A

Reason (if applicable): Reflect updates

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: _____ Date: _____

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M - 3

ICP THEORY

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BY _____ DATE _____

I. THEORY

Samples requiring analysis for numerous elements of interest may be analyzed by the inductively coupled plasma (ICP) method. Other factors for choosing ICP include matrix (soils, waters, oils), detection limits 0.005ppm - 0.5ppm), and EPA (or other) regulations.

This method uses argon as a carrier gas. The sample solution is introduced into the gas by means of a nebulizer The solution is desolated, decomposed, and atomized in the hot argon plasma.

Light emitted from the excited atoms is directed through a grating. Light intensities at various specific wavelengths are measured by a series of photo multiplier tubes These light impulses are converted to electrical energy and emission values are converted to concentration by a computer.

II. METHOD

Turn on the instrument and all ancillary equipment (computer, auto-sampler, etc...). Open argon valve and regulate gas flow.

Light the torch and allow the instrument to warm-up for no less than 30 minutes. The instrument will then be ready for profiling.

Profiling is the setting up and maintaining of precise optical alignment.

Using the computer terminal enter the name of method to be used. Then set the system for manual profile.

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ICP THEORY

Turn the mercury lamp to the vertical position and set the front panel meter to maximum reading.

Enter 100 into computer as the maximum intensity. Set the spectrometer by selecting a reference point of 70% of the maximum reading on the meter.

Set the low and high values by rotating the micrometer to reposition the optical grating, and read the front panel meter.

Enter these values into the computer. The computer will calculate an average value and display the correct micrometer setting. Rotate the micrometer to this setting.

The computer will then display a graphic profile for a mercury reading on the monitor.

The instrument is now ready to run for sample analysis. A 10ppm standard is now run to calibrate the instrument. This cover most elements of interest. For samples require analysis for Ca. Na. Mg, and/or K. A 50ppm standard is used. Analysis for ag and/or Sb requires a 1.0ppm standard.

Samples are introduced into the system by an auto-sampler or may b e fed directly into the peristaltic pump.

Sample results are printed on hard copy print-outs by the computer system. This raw data is then calculated by the analyst and recorded on bench sheets.

Bench sheets are then reviewed by group leader and passed along to data entry.

SOP Correction FORM

SOP Number: 11-10-13.0

SOP Title: ICP Theory

Page #: 2 of 2

Requested by : [illegible] Date: 12/3/92

Correction: A blank is analyzed before analyzing initial/ccb standards.

Reason (if applicable): _____

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: [illegible] Date: 12-3-92
100892

HERITAGE LABORATORIES, Inc.

SOP Correction FORM

SOP Number: M-10-13 0

SOP Title: ICP Theory

Page #: 1

Requested by : Dave C Date: 1-6-94

Correction: Add SW 846 6010A

Reason (if applicable): Reflect updates

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: _____ Date: _____
100892

DRAFT

M - 9

CVAA: MERCURY DETERMINATION IN WATER AND SOLID SAMPLES

I. THEORY

Cold vapor atomic absorption methods are used to determine mercury concentrations in solution. Concentration is measured in ug/l or parts per billion, with detection limits as low as 0.0002ppb.

As Hg is the only element of interest, the method uses a hollow cathode lamp which emits light at a wavelength of 253.7nm.

The light beam is directed through a flow cell of clear glass. The flow cell is cylindrical in shape with two open outlets through which sample vapors pass. The vapor is passed through the cell by means of a small air pump connected to an aerator.

Hg is held in solution through preparation using HNO_3, H_2SO_4, and $KMNO_4$ and _____. The Hg is then released into the closed flow cell system through an aerator placed in BOD bottle with sample. Stannous chloride is used to release Hg into vapor. As vapor containing Hg passes through the flow cell, mercury atoms will absorb light from the HCL.

Light passing onto the detector will be measured to calculate for an absorbance reading. Absorbance readings are entered into a calculator which is programmed with a curve from readings of a series of standards of known concentrations. In this way any absorbance value within this range may accurately be converted to concentration value.

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BY _____ DATE _____

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II. METHOD

Switch power on to instrument and all ancillary equipment.

Check the lamp current, adjust to 06 if not correct. Inspect all tubing connected to flow cell, pump and aerator, replace if cracked or badly discolored.

Adjust position of flow cell to obtain lowest absorbance value possible with aerator in DI water.

Prepare a 10ppm Hg standard from 1000 ppm stock. Using the 10ppm standard prepare a 0.10ppm spike solution. Both standards should be preserved with 1% HNO_3 and 1% $KMNO_4$.

Prepare reductant solution number 1, dissolve 60g of NaC1 and 60g hydroxylamine hydrochloride into 100-200ml of DI and dilute to 500ml.

Prepare reductant solution number 2, dissolve 50g of $SnSO_4$ or $SNCl_2$ into 100-200ml of DI. Add 7ml of concentrated H_2SO_4 and dilute to 500ml. Keep solution on a stir plate and provide constant stirring during use.

Prepare several blanks and a series of standards. Standard concentrations are 0.20ppb, 0.50ppb, 1.0ppb, 2.0ppb, 3.0ppb and 5.0ppb.

Fill 1 BOD bottle with 100ml of DI, 1 BOD bottle with 100ml $KMNO_4$. The $KMNO_4$ will act as a trap for Hg vapor. After reading sample absorbencies. The reductant will clean $KMNO_4$ from aerator and the DI water serves as a final rinse before aerator is placed into next sample.

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CVAA

All standards, blanks and samples are read in the following manner:

Add 6.0ml of reductant #1 to sample container. Swirl bottle to dissolve all $KMNO_4$.

Add 5.0ml of reductant #2 and insert aerator into BOD bottle immediately. Observe absorbance reading on digital display and record on bench sheet.

Read a blank and calibration standards before any samples. Calibrate a curve on a TI-60 calculator, plotting standard concentration and respective absorbance values (see MG SOP M-5).

Mark print-out from chart recorder with sample numbers, QC information, dilution and/or prep factors, absorbance values and concentration values.

Read a BLAO1, ICVO1 and CCV before first set of samples. Be sure to include BLAO2, LCS, SPIO2, DVPO2 or DSPO2 with each prep set.

Read all samples and spikes for 1 pt or 3 pt MSA leachates, making certain all prep QC is run with prep sets.

Water samples with detectable concentrations of Hg (above detection limits) must be re-analyzed to eliminate doubt of contamination in BOD bottles. Record these sample numbers on a separate list to ensure re-analyization.

Finish each set of 10 samples with another BLAO: and CCV. End the run with a BLAO1, ICV01 (EPA) and CCV (Same source as calibration standards).

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CVAA

Calculate concentrations and spike recoveries, remembering to multiply raw values by dilution or prep factors. (i.e. 2g/50ml = factor of 25; 1:10 dilution = factor of 10).

Record all results on bench sheets. Record linearity, Y intercept, characteristic concentration and slope on a numbered cover sheet. Re-check bench sheets for completeness, include sample number, QC information, volume or weight prepped, detection limits and raw absorbance values.

Turn completed paper work into group leader or supervisor for review.

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MERCURY SAMPLE PREPARATION FOR ANALYSIS BY CVAA
(SW 846 7470 & 7471, EPA 245.1, CLP-M 245.5)

Submitted by: Ron Byers

Title: Trainer, Metals Section

Approval

Date 5-21-93

PURPOSE: This document describes the procedures used to prepare aqueous, solid, oil and leachate samples for analysis by Cold Vapor Atomic Absorption. This SOP replaces M-10-20.1.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory. The reference methods are SW 846 7470 & 7471, EPA 245.1 and CLP-M 245.5.

PROCEDURE:

I. **PERSONNEL:** All Metals Section personnel involved in preparing samples for analysis by CVAA will be trained to adhere to these methods. Training will be conducted by the Metals Section Trainer or by a fully qualified designee. Training will be documented on the appropriate training forms.

II. **FACILITIES:** These procedures are to be performed in the Metals Prep Laboratory.

III. **SAFETY:** All normal safety apparel must be worn while performing this procedure. This includes safety glasses, gloves and a lab coat. As an added precaution, a face shield must be worn while adding reagents to samples. All reagents must be added in an operating fume hood.

IV. **EQUIPMENT:** Equipment used to perform these procedures includes a fume hood, graduated cylinders, an analytical balance, BOD bottles with ground glass stoppers, a water bath and various pipettors.

V. **MATERIALS:** Nitric acid (HNO_3) and Sulfuric acid (H_2SO_4) used in this procedure are analytical reagent grade. Potassium permanganate ($KMnO_4$) must be analytical grade and "APHA for Mercury". Potassium persulfate ($K_2S_2O_8$) must be analytical reagent grade. Deionized water is used for blanks and final dilutions of samples. All acids must be stored in designated storage areas or kept in repippettors in the fume hood. No acid is to be used past the expiration date on the container.

Spiking solutions and laboratory control samples are prepared by the analyst daily. Spiking solutions and laboratory control samples are stored in designated containers. No spiking solution or laboratory control sample is to used after the date on the

container(s). See Section VII a. for preparation and concentration requirements of spiking solutions.

I. SAMPLE REQUIREMENTS: Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers. Glass containers are preferred. All aqueous and leachate samples MUST be preserved with nitric acid to a pH < 2.0. Sample volume must be sufficient to support this digestion and all other metals analyses required.

Holding time for samples is 28 days in glass containers (13 days in plastic). Sample disposal is to be done at 30 days from the date of the final report unless a longer period is specified by the client. Check with the metals section prep supervisor before disposing of any samples.

II. DIGESTION PROCEDURES:

a. **Spiking and Preparation Solutions:** Two separate spiking solutions are used in all Mercury sample preparations. The first is prepared from Fisher 1000 ppm stock (or the equivalent) and is used to spike matrix spike (SPI02 and DPS02) samples (it is also used to spike all calibration and continuing verification standards at the instrument). The second is prepared from Inorganic Ventures 1000 ppm stock (or the equivalent) and is used to spike LCSs (it is also used to spike ICVs at the instrument). Prepare spiking solutions to be used in the following manner:

Rinse all 4 volumetric flasks (2 - 25 ml & 2 - 100 ml) designated for spiking solution preparation with concentrated HNO_3 and rinse at least 3 times with DI water. Fill each of the flasks approximately half full with DI and 1 ml of concentrated HNO_3 and 1-2 ml of $KMnO_4$ to each flask. Add 250 μl of the appropriate 1000 ppm stock to the 25 ml flasks and dilute to volume. Decant the diluted (10 ppm) solution into a small plastic bottle and label with concentration, source (i.e. Fisher or IV), date and analyst initials.

Add 1 ml of the 10 ppm solution to the appropriate 100 ml flask and dilute to volume. This will result in a 0.1 ppm (0.10 $\mu g/ml$) spiking solution. Transfer the solution to a labelled (see above) small plastic bottle. To prepare the potassium persulfate solution used in sample digestion, fill a 1000 ml volumetric flask half full of DI water and add 50g of potassium persulfate. Dilute to volume, add a stir bar and stir while heating gently until completely dissolved.

b. **Aqueous samples:** Each set of 10 or fewer samples must contain 1 prepped blank (BLA02-100 ml DI), 1 laboratory control sample (LCS-100 ml DI + 3 ml IV 0.1 ppm spike), 1 duplicate (DUP02) and a spiked sample (SPI02-100 ml sample + 1 ml of Fisher 0.1 ppm spike). Some clients request a DPS02 (100 ml sample + 1 ml Fisher 0.1 ppm spike). Using a 100 ml graduated

cylinder, transfer a 100 ml aliquot of well mixed sample to the BOD bottle and label the bottle with the sample number. Add 2.5 ml of concentrated HNO_3, 5 ml of concentrated H_2SO_4 and 15 ml $KMnO_4$ to each BOD bottle. Wait 15 minutes to make sure that all samples are holding the purple color. If any sample(s) do not maintain the color for 15 minutes, add $KMnO_4$ in 5 ml increments until the sample holds the color for 15 minutes. Document all additional $KMnO_4$ used (after 15 ml initially added) on prep sheet.

Add 8 ml of $K_2S_2O_8$ to each bottle and seal with a stopper. Place bottles in the water bath and digest at 95°C for 2 hours. Remove bottles from the bath and cool to room temperature before analysis.

Some samples may require dilution. Document all dilutions on the bench sheet and label bottle with dilution. Aqueous samples which are HLI matrix 5 must prepped on a weight to volume basis. Weigh a portion of well mixed sample (see the Prep Supervisor if you have questions about amounts) into a BOD bottle, dilute to 100 ml and prep following the aqueous digestion procedure described above.

c. **Leachate samples:** Each set of 10 or fewer samples must contain 1 prepped blank (BLA02-100 ml DI), 1 LCS (use same concentration as aqueous prep) and 1 duplicate sample (DUP02).

TCLP matrix bias spikes are considered to be separate samples and are spiked by the technician doing the final filtration of TCLP samples. Using a 100 ml graduated cylinder, add 90 ml of DI to each BOD bottle to be used for leachate sample digestion. Label each bottle with sample number and dilution (normally 1:10). Transfer 10 ml of sample or TCLP spike sample (use a 10 ml macro pippettor) to the appropriate BOD bottle. Add 2.5 ml of HNO_3, 5 ml of H_2SO_4 and 15 ml of $KMnO_4$ to all bottles. Wait 15 minutes as described in the aqueous sample digestion procedure above. Add 8 ml of $K_2S_2O_8$ and place the sample bottles in the water bath and digest at 95°C for 2 hours. Remove bottles from the bath and allow to cool to room temperature before analysis.

d. **Solid and organic samples:** Each set of 10 or fewer samples must include 1 BLA02, 1 LCS, 1 DUP02 AND 1 SPI02. Organic TCLP samples or organic phases of TCLP samples are also digested following this method. Weigh a 0.40g aliquot of well mixed sample into a BOD bottle. A 0.40g subsample is used in place of a 0.20g subsample (CLP 245.5) to achieve the lower detection limits required by many clients. Label each bottle with sample number and dilution (wt/vol.). If sample matrix or other concerns warrant, other initial weights may be used (refer any questions to trainer or supervisor). Document any deviations on the bench sheet and sample bottle. Add 5 ml of H_2SO_4 and 2.5 ml of HNO_3 (as per CLP 245.5), close with stoppers and sonicate for 5

minutes to dissolve solids in acid. Heat samples in preheated water bath for 2 minutes at 95°C.

Cool the samples and add 50 ml of DI. Add 15 ml of $KMnO_4$ and 8 ml of $K_2S_2O_8$ to each bottle. Place samples in the water bath and heat at 95°C for 30 minutes. Cool samples to room temperature and add an additional 50 ml of DI before analysis.

Quality Control: All samples are to prepared in the exact same manner, following Standard Operating Procedure. All requirements of the Heritage Laboratories COMP. QAP must also be met. Every effort must be made to ensure a homogeneous representative subsample is used for each sample within the set to provide accurate and reproducible results. If any deviation from SOP is indicated by sample matrix or safety concerns, contact the Metals Group Leader or Prep supervisor before beginning digestion. All matrix spike solutions must be added prior to digestion. All Laboratory Control Samples, Duplicate samples and Blanks must be completely digested at the same time as all other samples within the set. All samples within a set must be digested on the same hot plate whenever possible.

Care must be taken to document every sample digestion procedure accurately on the bench sheet. Document any abnormalities in reaction, sample matrix or physical properties observed during digestion or filtration. Carefully select and record quality control samples (some clients require QC samples from each set of samples they submit) on bench sheet. Record all volumes and all lot numbers of spike solutions and standards.

Do not forget the importance of accuracy in documentation of sample numbers, sample weights and volumes, dates, analyst identification and methodology practiced.

DOCUMENTATION: All samples must be documented on a "stepped" prep bench sheet. These bench sheets are prenumbered by the Data Entry staff and contain all Run numbers and Qc numbers. Sample numbers, QC sample numbers, initial and final volumes, due date(s), elements of interest and analytical codes are recorded on the bench sheet.

Prep code, date, analyst initials and employee number are recorded in the upper left hand corner of the bench sheet.

Original bench sheets are given to the Metals Prep Supervisor. A copy of the bench sheet is placed in a logbook to be kept at the bench for easy reference.

These procedures were developed specifically for use by HERITAGE LABORATORIES INC. and may not be applicable for other organizations.

EMS Test Codes: P101.3, P101.4, P101.5
Method Cuote: EPA 335.2 (Titrimetric, Spectrophotometric)

CYANIDE DISTILLATION

Referenced Procedures - (USEPA Method 335.2, Standard Methods 4500-CN C., USEPA Method SW846-9010)

I. Introduction

This method is applicable to the determination of cyanide in drinking, surface, and saline waters, domestic and industrial wastes. Cyanide is common to many industrial processes. Because of its high toxicity and reactivity, cyanide is of major environmental concern. Cyanide, defined as cyanide ion and complex cyanides, is converted to hydrocyanic acid (HCN) by reaction in a reflux system (distillation apparatus) of a mineral acid in the presence of magnesium ion. All soil samples and most water samples to be analyzed require distillation to remove interferences and to break down tightly bonded cyanide complexes.

A. Test - P101.3 (EPA 335.2)
P101.4 (SW846-9010)
P101.5 Leachate (SW846-9010)
B. Method Detection Limit - .01mg/L
C. Containers - Plastic or glass bottles
D. Preservatives - 2 mL 10N NaOH per liter of sample, refrigeration at 4°C
E. Regulatory Holding Time - 14 days
F. Recommended Holding Time - 14 days

II. Extraction Procedures

A. Theory

Summarizing the method, cyanide as hydrocyanic acid (HCN) is released from cyanide complexes (as a gas) by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

B. Apparatus
1. Reflux distillation apparatus as shown in Figure 1.
2. Flat-bottomed flask 1000 mL, with inlet tube and provision for condenser.
3. Heating mantle - adjustable
4. Tygon tubing - anywhere after the scrubber
5. Teflon tubing - between the condenser and the scrubber
6. Vacuum pump
7. Lead acetate paper

C. Reagents
1. Sodium hydroxide solution 1.25N
Dissolve 50g of NaOH in distilled water in a 1L

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BY_____ DATE_____

SOP Correction FORM
HERITAGE LABORATORIES, INC

SOP Number: Old Format

SOP Title: Cyanide Distillation

Page #: 1

Requested by : Barb Shrake Date: 1/4/94

Correction: Under I. Introduction . . . Subheading A. Test P101.4 (SW846-9010) change to P101.4 (SW846-9010A)

Reason (if applicable): Method update

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager Signature: Gary A. Klopfer Date: 1/6/94

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volumetric flask and dilute to the mark.

2. Sulfuric acid (1+1)
3. Magnesium chloride (MgCl) solution
   Weigh 510g of $MgCl_2 \cdot 6H_2O$ into a 1L volumetric flask. Dissolve and dilute to 1 liter with distilled water.
4. Sulfamic acid
5. L-Ascorbic acid
6. Acetic acid
7. Lead carbonate
8. Lead acetate solution
   Weigh 30g PbOAc into a 1L volumetric flask. Dissolve and dilute to the mark with DI water. Add enough acetic acid to obtain a pH of 4.5.

D. Procedure

1. Determine if samples contain sulfide (interference) by testing with lead acetate paper. If samples do contain sulfide proceed as follows:
   a. Add approximately 2g of lead carbonate to the water sample. The lead carbonate will precipitate the sulfide. Test the sample again with lead acetate paper. If sulfide remains, add 2g more of $PbCO_3$. Continue this until no sulfide is present.
   b. Filter the sample into the boiling flask for distillation.

   *<u>NOTE</u>: Soil samples which contain sulfide cannot be filtered since cyanide particles will adhere to suspended material. Therefore, for all soil samples containing sulfide, add an additonal scrubber to the distillation set up. This scrubber solution should consist of 50 mLs lead acetate (PbOAc) with enough DI water to cover the bubbler. Place this scrubber in the set up <u>before</u> the NaOH scrubber. Make sure the lead acetate solution is not basic.

2. Place 10g of a solid sample or 250 mL of water into a 1000 mL boiling flask.
3. Add 50 mLs of 1.25N NaOH to scrubber, and add about 100 mL DI water to cover bubbler.
4. Remove additional interferences from sample.
   a. Add 2g sulfamic acid to remove NO_2^- and NO_3^- interference.
   b. Add 2g L-ascorbic acid to remove residual chlorine interference.
5. Turn on vacuum pump and connect the distillation system, consisting of boiling flask air inlet, flask, condenser, vacuum, and scrubber. Adjust the suction so that approximately 1 to 2 air bubble/sec enters the boiling flask.

NOTE: Observe the air purge rate in the absorber. The smaller the bubbles the better in order to achieve maximum contact with the scrubber solution. To make the bubbles smaller, tilt the scrubber at an angle.

6. After closing the system, add 40 mLs of magnesium chloride solution (Reagent 3.) to the boiling flask through the thistle tube. Wash down with DI water.
7. Carefully and slowly add 40 mLs of (1+1) H_2SO_4 (again down thistle tube) and follow with a rinse of DI water.
8. Heat with rapid boiling, but do not flood condenser inlet or permit vapors to rise more than halfway into condenser. Reflux for 1 hour, after the sample starts boiling.
9. At the end of one hour, discontinue heating but continue air flow for 15 minutes. Allow sample to cool adequately.
10. Bring caustic scrubber to volume (250 mL) to prepare for analysis.
11. Put scrubber solution into bottle and label with sample number, initial wt/vol, final volume, run number, and mantle number.

III. Analysis Procedure

Not Applicable

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

QAQC samples are done per cyanide distillation run as follows:

Method Prep Blank (BLA02)- one per every 15 samples
Laboratory Control Sample (LCS02)- one per every 7 samples
Matrix Spike (SPI02)- one per every 15 samples
Matrix Duplicate (DUP02)-one per every 7 samples

All cyanide distillation prep data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Not Applicable

VI. Interferences/Troubleshooting

Oxidizing agents such as chlorine, decompose most cyanides. Residual chlorine is removed from samples by the addtion of L-ascorbic acid.

Oxidized products of sulfide convert CN^- to SCN^- rapidly, especially at high pH. Sulfide found in the samples can be eliminated by adding lead carbonate.

Carry-over between samples prepped on the same distillation position occurs when high cyanide samples are encountered. To avoid this problem, run all water samples first, followed by soil samples which usually have higher concentrations of cyanide. In addition to this, make sure to label sample bottles with the run number and mantle number they were prepped on so that they can be tracked for possible sources of carry-over.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. Cyanide preparation should be done with the utmost care since many of the chemicals are toxic or corrosive.

VIII. Clean Up and Disposal

All glassware should be cleaned with soap and hot water. Rinse with DI water. Wash condensors and tubing with NaOH (0.25N) and with (1+1) H_2SO_4 and rinse with DI water.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 335.2.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 4500-CN.

U.S Environmental Protection Agency, Method SW846-7.3.3.2

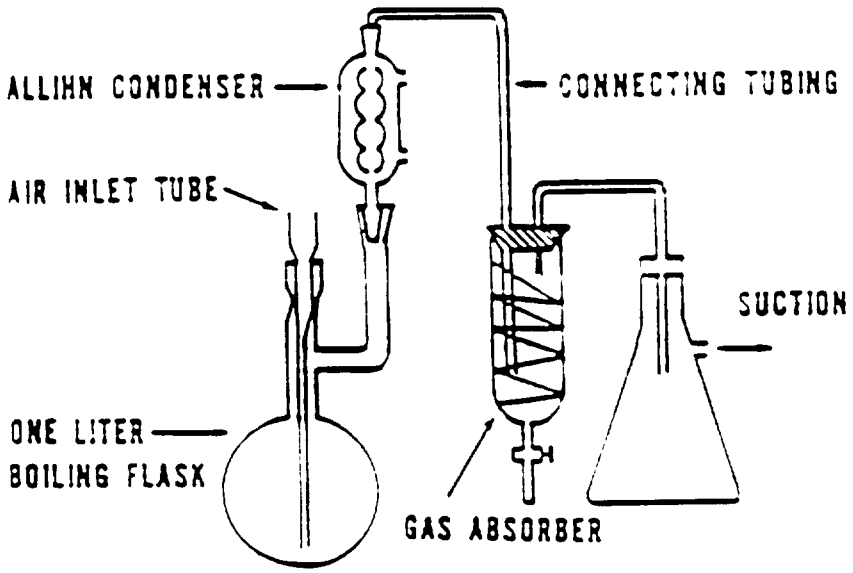

FIGURE 1

CYANIDE DISTILLATION APPARATUS

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BY _____ DATE _____

EMS Test Codes: G111.3, G111.4
Method Quote: EPA 335.1 (Titrimetric, Spectrophotometric)

CYANIDES, AMENABLE TO CHLORINATION

Referenced Procedures - (USEPA Method 335.1, Standard Methods 4500-CN G., USEPA Method SW846-9012)

I. Introduction

This method is applicable to the determination of cyanides amenable to chlorination in drinking, surface, and saline waters, domestic and industrial wastes. Cyanide is common to many industrial processes. Because of its high toxicity and reactivity, cyanide is of major environmental concern.

The chlorination test procedure is carried out under rigorous conditions appropriate for measurement of the more dissociable forms of cyanide. This test is often required by treatment facilities to determine the amount of cyanide that can be destroyed by the addition of chlorine.

A. Test - G111.3 (EPA 335.1)
G111.4 (SW846-9012)
P111.2 (Cyanide Amenable Distillation - EPA 335.1)
P111.4 (Cyanide Amenable Distillation - SW846-9010)
B. Method Detection Limit - .01mg/L
C. Containers - Plastic or glass bottles
D. Preservatives - 2 mL 10N NaOH per liter of sample, refrigeration at 4°C
E. Regulatory Holding Time - 14 days
F. Recommended Holding Time - 14 days

***NOTE**: The cyanides amenable to chlorination test is only performed if the result for total cyanide is detected.

II. Extraction Procedures

A. Theory

Summarizing the method, a portion of the sample is chlorinated at a pH >11 to decompose the cyanide. Free cyanides are destroyed by the free chlorine generated. Remaining cyanide levels in the chlorinated sample are then determined by the method for Total Cyanide (see Total Cyanide SOP). Cyanides amenable to chlorination are then calculated by difference.

B. Apparatus
1. 600 mL beaker
2. Stir plate
3. Potassium Iodide (KI) starch paper
4. pH Paper

C. Reagents

1. Sodium hydroxide solution 1.25N
   Dissolve 50g of NaOH in distilled water in a 1L volumetric flask and dilute to the mark.
2. Calcium hypochlorite
3. L-ascorbic acid

D. Procedure

1. Measure 250 mL of water sample, (or 10g of soil sample to 250 mL) into an "open" 600mL beaker.
2. Adjust pH to between 11-12 with 1.25 N NaOH.
3. Place the beaker on a magnetic stirrer plate for constant stirring during the reaction.
4. Add calcium hypochlorite to the beaker and continue until KI-starch paper turns blue indicating excess of free chlorine.
5. Check every 15 min. over a period of an hour maintaining pH and chlorine.
6. After one hour, add 0.5g portions of L-ascorbic acid until KI paper shows no residual chlorine (no blue color). Add and additional 0.5g of ascorbic acid to insure the presence of excess reducing agent.
7. Distill the amenable cyanide as any other sample for cyanide analysis (see Cyanide Distillation SOP).

III. Analysis Procedure

Not Applicable

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

Matrix spikes and standards are not applicable to this prep. QAQC samples are done per cyanide amenable distillation run as follows:

Matrix Duplicate (DUP02)-one per every 10 samples

All cyanide amenable distillation prep data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Calculate the cyanide amenable to chlorination as follows:

$$CN\ mg/L = A - B$$

where:
A = mg/L total cyanide in unchlorinated aliquot
B = mg/L total cyanide in aliquot treated by chlorination

VI. Interferences/Troubleshooting

Some unidentified organic chemicals may oxidize or form breakdown products during chlorination, giving higher results for cyanide after chlorination than before chlorination. This may lead to a negative value for cyanides amenable to chlorination after distillation for wastes from, for example, the steel industry, petroleum refining, and pulp and paper processing. Negative values are also often obtained for samples containing significant quantities of iron cyanides.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. Cyanide preparation should be done with the utmost care since many of the chemicals are toxic or corrosive.

The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride. It is recommended that this reaction be performed in a fume hood.

VIII. Clean Up and Disposal

All glassware should be cleaned with soap and hot water. Rinse with DI water.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 335.1.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 4500-CN G.

EMS Test Codes: G101.3, G101.4, G101.5
Method Quote: EPA 335.3 (Colorimetric, Automated UV)

TOTAL CYANIDE ANALYSIS

Referenced Procedures - (USEPA Method 335.3, Standard Methods 4500-CN E., USEPA Method SW846-9012)

I. Introduction

This method is applicable to the determination of cyanide in drinking, surface, and saline waters, domestic and industrial wastes. Cyanide is common to many industrial processes. Because of its high toxicity and reactivity, cyanide is of major environmental concern.

Cyanide as hydrocyanic acid (HCN), is released from cyanide complexes as a gas by means of distillation. When total cyanide is determined colorimetrically), the almost condissociable cyanides, as well as cyanide bound in complexes that are readily dissociable and complexes of intermediate stability, are measured.

A. Test - G101.3 (EPA 335.3 - Automated)
G101.4 (SW846-9012 - Automated)
G101.5 Leachate (SW846-9012 - Automated)
B. Method Detection Limit - .01mg/L
C. Containers - Plastic or glass bottles
D. Preservatives - 2 mL 10N NaOH per liter of sample, refrigeration at 4°C
E. Regulatory Holding Time - 14 days
F. Recommended Holding Time - 14 days

II. Extraction Procedures

A. Theory

Summarizing the method, cyanide as hydrocyanic acid (HCN) is released from cyanide complexes (as a gas) by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. Cyanides are converted to cyanogen chloride by reactions with chloramine-T which subsequently reacts with pyridine and barbituric acid to give a red-colored complex. The complex is then measured colorimetrically at 570 nm.

B. Apparatus
1. Auto analyzer instrument (AAII - Technicon)
2. Automatic sampler
3. Proportioning pump
4. Heating bath/mini distillation apparatus capable of heating to 150°C
5. Colorimeter equipped with:
   a. interference filter: 570nm
   b. flow cell: 15mm

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6. Chart recorder
7. Plastic sample cups

C. Reagents

1. Distillation reagent

Carefully add 250 mL of 85% phosphoric acid (H_3PO_4) and 50 mL of hypophosphorus acid to 700 mL of DI. Mix and dilute to 1L with DI water. Prepare weekly.

2. Phosphate buffer, ph=5.2

Dissolve 13.6g of potassium dihydrogen (KH_2PO_4) and 0.28g of disodium hydrogen phosphate (Na_2HPO_4) in 900 mL DI water and dilute to 1L. Prepare weekly.

3. Chloramine-T

Dissolve 2.0g of chloramine-T in 500 mL DI water. Prepare <u>daily</u>.

4. Pyridine barbituric acid reagent

CAUTION: Prepare this reagent under a fume hood.

Weigh 15g of barbituric acid into a 1L beaker. Wash the sides of the beaker with about 100 mL of DI water. Add 75 mL of pyridine and mix. Add 15 mL of conc HCl and mix. Dilute to about 900 mL with DI water and mix until all of the barbituric acid has dissolved. Transfer the solution to a 1L volumetric flask and dilute to the mark. Store this reagent in a glass container and prepare weekly.

5. Sodium hydroxide 1.25 N

Dissolve 50g of NaOH in 500 mL DI water and dilute to 1L.

6. Stock Cyanide Solution 100mg/L

Weigh 0.250g potassium cyanide (KCN) into a 1L flask. Dilute to the mark with 0.1 N NaOH.

*<u>**NOTE**</u>: All working standards should contain 20 mL of 1.25N NaOH per 100 mLs.

D. Procedure

Some drinking water samples are run without distillation, however most samples must be distilled prior to analysis (see cyanide distillation SOP). All soil sample distillates are diluted 1:100 to screen for high cyanide content.

III. <u>Analysis Procedure</u>

A. Theory

Continuous flow analysis (CFA) is based on injection of a liquid sample into a moving segmented carrier stream of a reagent. Intermixing of individual samples and sample dispersion in the stream is prevented by air bubbles placed between samples. The AAII instrument basically consists of a pump that propels the carrier stream, a heating bath/mini distillation apparatus where the sample is heated to 150°C and distilled before actual analysis, and a module with sampl coils in which the sample is mixed with the components of the carrier stream (buffer, chloramine-T, and color reagent). This

mixing forms a colored species which is sensed by the flow through detector (570nm). The signal being detected is seen as a peak, the height of which is related to the concentration of analyte. The actual peak is recorded on a chart recorder device.

Using this CFA technique, cyanide in drinking, surface, and saline waters and domestic and industrial wastes, can be determined over a range of 0.01 to 0.45 mg/L on the AAII. The range may be extended with sample dilution. One sample tray (40 sample cups) can be run in 1 hr. 15 min. (blank cups are run in between each sample).

B. Method

1. Instrument setup

Before operating the AAII instrument, several things need to be checked. Make sure the carrier and wash reagent bottles are filled sufficiently with DI water. Check both the buffer solution and the color reagent bottles to assure they are adequately filled for a run and that they have been recently made up. If any particulate matter is seen in the bottles, make up fresh reagent (prepare new reagents each week).

Inspect all pump tubing to make sure there are no obstructions in the lines and that none of the tubing needs to be replaced. Plug in heating bath and allow to heat up to 150°C. Raise tension levers on pump tube cassettes and place reagent feedlines in a beaker of DI water to flush the system while the heating bath is warming up. After this, place reagent feedlines into proper containers and allow reagents to pump through the system.

Turn on power of sampler and detector. The detector should warm up for at least 15 minutes prior to analysis. Establish a stable baseline before analyzing standards or samples.

2. Initial conditions and calibration

When system has reached equilibrium, run 4 standards (0.30mg/L) to assure that the instrument is set correctly. If necessary, adjust the instrument (Std Cal knob) to the proper reading according to the 0.30 mg/L standard.

In addition to the 4 initial standards and after the standard curve, run a CRDL sample at 0.01mg/L to insure instrument detection limit.

A set of six working solutions are used to calibrate the cyanide method. Into five 100 mL volumetric flasks pipet, respectively,

0.45, 0.40, 0.30, 0.20, and 0.10 mL

of the working cyanide stock solution (Reagent 6.- 100 mg/L). Dilute to the marks with 20 mL 1.25N NaOH and DI water. This makes

0.45, 0.40, 0.30, 0.20, and 0.10 mg CN/L

respectively. A blank is used as the sixth calibration standard.

Place calibration standards in sample tray in descending order of concentration. Load unknown samples into even sample positions to be run following calibration with DI blanks in the odd positions. The sample rack should not be processed until a calibration curve has passed (corr. coeff. ≥0.999).

3. Instrument shutdown

At the end of the run, first place all feedlines into a wash DI water container. Leave the proportional pump on and turn off the heating bath. Allow to cool until it is no longer distilling. Flush the system for approximately 15-20 minutes. Turn off the pump and release tension levers on pump tube cassettes. The instrument power switches can then be turned off.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. A start-up test of the instrument in use is done to establish the laboratory's ability to set up and operate the analytical equipment and procedures. The purpose is to prove that the analytes of interest can be detected under the parameters set forth and that the analyst can identify the analytes. This includes a detection limit determination which is performed both when a new analysis is first begun, and at timely intervals while the instrument is up and functioning. Both instrument and method detection limits are determined at this time.

To further assure the representativeness of data produced for the AAII instrument internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix duplicates.

Instrument QAQC samples are done per run as follows:

Method Prep Blank (BLA01)- one per run

Laboratory Control Sample (LCS01)- one at beginning and one at the end of the run

Continuing Calibration Verification - one per 10 samples

Matrix Spike (SPI01)- one per 20 samples-with 80-120% recovery

*NOTE- Add 0.2 mLs of 100mg/l solution to a volumetric flask and dilute to the mark with sample.

Matrix Duplicate (DUP01)-one per 10 samples-with replicability <= 20%

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

Sample QAQC from the distillation prep is also run including SPI02's, DUP02's, BLA02's, and LCS02's (see cyanide distillation SOP).

All cyanide data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Prepare a standard curve by entering concentration values (x-axis) vs. peak heights (y-axis) into the TI-60 or TI-55 calculator. The following sequence of keys is used to prepare the curve:

1. conc. of std (mg/L)
2. [x*y]
3. peak height
4. [Σ+]
5. Repeat steps 1-4 for all six standards
6. [2nd][Corr] calculates correlation coefficient
7. [2nd][Slope] calculates slope of curve
8. [2nd][Intcp] calculates intercept of curve

Record the correlation coefficient, slope and intercept on the calculation sheet for documentation purposes. The correlation coefficient must be ≥0.998 for acceptance.

To calculate sample concentrations enter the sample peak height into the standard curve [2nd][x]. This will give the concentration of the sample in mg/L (mg/kg for soils). Multiply the result (as well as the detection limit) by any dilution factors. For soil samples (10g to 250 mLs) the result must be multiplied by 25 for the 1:25 dilution.

VI. Interferences/Troubleshooting

All known interferences are eliminated or reduced to a minimum by distillation.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves.

CN^- in the alkaline distillate is converted to CNCl by reaction with chloramine-T. CNCl is a toxic gas: avoid inhalation.

Individual cyanide standards are extremely toxic. Cyanide is fast acting, and highly poisonous by ingestion. It can enter the body through the skin or by inhalation. Overexposure can cause headache, weakness, ineffective breathing, and nausea.

KCN is alkaline and thus irritating and corrosive to body tissue it contacts. Avoid contact with skin or clothing.

VIII. Cleanup and Disposal

Samples can be disposed of into the sink, rinsing with copious amounts of water. Cups can be placed in the garbage can.

Make sure to put lids on all reagent bottles and calibration flasks when finished.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 335.3.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 4500-CN E.

U.S Environmental Protection Agency, Method SW846-9012.

SOP Correction

SOP Number: OLD FORMAT

Requested by : CHRIS BOYLE Date: 10-28-92

SOP Title: CYANIDE (TOTAL)

Page #: 2

Correction: UNDER II. C. 6
THE STOCK CYANIDE SOLUTION SHOULD BE
STANDARDIZED WITH 0.0192 N $AgNO_3$.

APPROVAL

Laboratory Manager Signature: Gary A. Klingler Date: 10/29/92

SOP Correction FORM

SOP Number: CN-10-17.0

SOP Title: TOTAL CYANIDE ANALYSIS

Page #: 4

Requested by : Barb Shrake Date: 10/9/92

Correction: Under QA/QC:
Cyanide Calibration Working standard values are:
0.0, 0.01 0.03, 0.10, 0.20, and 0.30 mg/l.

Reason (if applicable):

Correction has been implemented (Y/N): Y Date : 10/9/92

Correction will be implemented by (date):

Correction will be included in next SOP revision by (date): 4/93

APPROVAL

Laboratory Manager
Signature: [signature] Date: 10/14/92
100892

ORIGINAL

pH DETERMINATION
(SW 846 9040,9045, EPA 150.1)

Submitted by: Ron Byers

Title: Trainer, Metals Section

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Approval

Date 5-21-93

BY _____ DATE _____

PURPOSE: This document describes procedures used to determine pH of aqueous, solid, organic and soil samples (calcareous and non-calcareous). This SOP replaces M-10-8.1.

POLICY: It is HERITAGE LABORATORIES policy to have a written Standard Operating Procedure for all methods practiced in the laboratory. The reference methods are SW846 9040, 9045 and EPA 150.1.

PROCEDURE:

I. **PERSONNEL:** All personnel involved in determination of pH will be trained to adhere to these methods. Training will be conducted by the Section Group Leader or by a fully qualified designee. Training will be documented on the appropriate training forms.

II. **FACILITIES:** This procedure may be performed in the laboratory or in the field.

III. **SAFETY:** All normal safety apparel must be worn while performing this procedure. This includes safety glasses, gloves and a lab coat. Always use a face shield and/or a fume hood for samples which are labelled acidic, caustic or explosive. Handle all samples with caution.

IV. **EQUIPMENT:** Equipment used to perform this procedure includes a pH meter capable of a readout to 0.01 pH in a range from 0.00 units to 14.00 units and a variety of electrodes to meet specific applications. Electrodes are designated for aqueous or solid/soil samples only. An automatic temperature compensation probe is also used for aqueous samples when sample temperature varies from ambient temperature.

V. **MATERIALS:** Calibration standards are Redbird buffer solutions or the equivalent (pH 4.00, 7.00 and 10.00). Initial Calibration Verification (ICV) standards are Baxter SRM or the equivalent and are obtained from the QA Unit (pH 4.00 and 7.00).

VI. **SAMPLE REQUIREMENTS:** Original sample containers vary from 120 ml plastic bottles to 1 liter Cubetainers. Glass containers of various sizes may also be used. All samples must be unpreserved. All samples must be kept at 4°C during shipment and handling. Aqueous samples may be allowed to warm to ambient temperature

before pH reading is taken. If aqueous samples are not allowed to reach ambient temperature Automatic Temperature Compensation probe must be used. (A pH temperature correction chart may be used if an ATC probe is not available.)

Holding time for samples is 24 hours and all aqueous samples MUST be done IMMEDIATELY UPON RECEIPT OF SAMPLES.

The Laboratory Section doing the pH determinations will supply the Shipping/Receiving with a list of qualified personnel (updated as the situation warrants). The Shipping/Receiving personnel will contact the appropriate Section personnel when samples are received, he/she will go to the Receiving area sign the Short Holding Time List and return to laboratory section with the samples for pH determination.

VII. pH DETERMINATION PROCEDURES:

a. Aqueous Samples: Turn on the pH meter and clear to remove previous calibration. Using the electrode designated for aqueous samples, calibrate the meter with 2 buffer solutions. If expected range of samples is between pH 4.00 and 7.00, use those buffer solutions. If expected range is above pH 7.00, then use 7.00 and 10.00 buffer solution to calibrate meter. To calibrate the meter, immerse electrode and automatic temperature compensation probe (ATC) in the lower pH buffer solution and press "pH" and STD on the meter. Allow the meter reading to stabilize. Rinse the electrode and ATC with deionized water, blot excess water and immerse in the higher standard. Press "STD" only and allow meter reading to stabilize.

If a different type of meter is used, calibrate according to the instructions supplied with the meter allowing for slope, intercept or other manual functions.

Read and record all 3 pH standards before reading any samples. To determine the pH of standards or samples immerse the electrode and ATC probe in the solution and press "pH' on the meter. Allow meter reading to stabilize and record result on the bench sheet. Read 4.00,7.00 and 10.00 buffer solutions and record on bench sheet.

Begin each set of 10 or fewer samples with an ICV and CCV. Complete each set with a duplicate reading and a CCV.

Rinse the electrode and ATC probe thoroughly with deionized water between each sample or standard and gently blot any excess liquid from the electrode.

Record all sample pH readings to the tenths place (i.e. 7.2 not 7.18). Record all QC pH readings to the hundredths place (i.e. 7.02 not 7.0). Record any sample readings above pH 13.00 as >13 and any below pH 1.00 as <1.

b. **Solids/Soils (Non-Calcareous):**

The pH meter is calibrated as in Section VII a. Use the electrode designated for solid samples. Weigh a 20g representative subsample into a beaker and add 20 ml of deionized water. Stir this mixture several (3-4) times during the next 30 minutes. Allow the solution to settle for 1 hour and read the pH of the aqueous phase of the solution. If 20 ml of deionized water is not sufficient to form an aqueous phase in the mixture, document the volume of any additional water needed on the bench sheet. To determine the pH of samples or standards immerse the electrode in the solution and press "pH' on the meter. Allow meter reading to stabilize and record result on the bench sheet. Read 4.00, 7.00 and 10.00 buffer solutions and record on bench sheet.

Begin each set of 10 or fewer samples with an ICV and CCV. Complete each set with a duplicate reading and a CCV. Rinse the electrode thoroughly with deionized water between each sample or standard and gently blot any excess liquid from the electrode. Record all sample pH readings to the tenths place (i.e. 7.2 not 7.18). Record all QC pH readings to the hundredths (i.e. 7.02 not 7.0). Record any sample readings above pH 13.00 as >13 and any below pH 1.00 as <1.

c. **Calcareous Soils:**

Prepare a 3.6 M solution of $CaCl_2$ by dissolving 1059g of $CaCL_2 \cdot 2H_2O$ in a 2000 ml volumetric flask with deionized water. Cool the solution, dilute to volume with deionized water and mix well. Dilute 20 ml of solution in a 1000 ml volumetric flask and bring to volume with deionized water. Deliver the 1000 ml dilution to the General Laboratory to be standardized (titration with $AgNO_3$ - see SW846 9045).

When molarity is determined by the exact titration, dilute 5.6 ml of the 3.6 M $CaCl_2$ solution to 2000 ml with deionized water. The resulting 0.01 M $CaCL_2$ solution must have a pH 5.00 and 6.50. The pH may be adjusted with a little $Ca(OH)_2$ or HCL. Also, deliver a 100 ml aliquot of solution to the General Laboratory to check specific conductivity (should be 2.32 +/- 0.08 mmho per cm at 25°C). Weigh 10 g of soil into a beaker and add 20 ml of 0.01 M $CaCl_2$ solution. Stir the mixture several (3-4) times during the next 30 minutes, then allow the suspension to settle for 30 minutes. Immerse the electrode into the solution just far enough to ensure good contact with the glass membrane, read and record the pH.

Report the results as "soil pH measured in 0.01 M $CaCl_2$". Begin each set of 10 or fewer samples with an ICV and CCV. Complete each set with a duplicate reading and a CCV. Rinse the electrode thoroughly with deionized water between each sample or standard and gently blot any excess liquid from the electrode. Record all sample pH readings to the tenths place (i.e. 7.2 not 7.18). Record all QC pH readings to the hundredths place (i.e. 7.02 not 7.0). Record any sample readings above pH 13.00 as >13 and any below pH 1.00 as <1.

d. **Hydrocarbons:** Calibrate the meter as described in Section VII a. Use the electrode designated for solid samples. Weigh a 20g representative subsample into a beaker and add 20 ml of deionized water. Stir the solution several (3-4) times during the next 30 minutes. Allow the solution to settle for 60 minutes. Using a disposable pipette, separate the oil phase from the aqueous phase. Discard the oil phase and take the pH of the aqueous phase. Follow all QC and documentation procedures described in Section VII a.

Quality Control: Sample sets will consist of 10 or fewer samples. Begin each set with an ICV and a CCV and end each set with a CCV. Lab duplicates must be performed at a frequency of 1 for each set of 10 samples. Matrix types are not mixed within sets. Separate CCV and DUP01 MUST be performed for each matrix type.

All samples are prepared in the exact same manner, following Standard Operating Procedure. Every effort must be made to ensure a homogeneous representative subsample is used for every 10 samples to provide accurate and reproducible results. If any deviation from SOP is indicated by sample matrix or safety concerns, contact the Metals Group Leader or designee before beginning pH determinations. Care must be taken to document every procedure accurately on the bench sheet. Document any abnormalities in reaction, sample matrix or physical properties observed during pH determination.

Carefully select and record quality control samples (some clients require QC samples from each set of samples they submit) on bench sheet. Record all lot numbers of standards.

Do not forget the importance of accuracy in documentation of sample numbers, sample weights and volumes, dates, analyst identification and methodology practiced.

DOCUMENTATION: All samples must be documented on a bench sheet. Sample numbers, QC sample numbers, initial and final volumes, due date(s) and analytical codes are recorded on the bench sheet. Prep code, date, analyst initials and employee number are recorded in the upper left hand corner of the bench sheet.

All reagents and prep solutions used are recorded in the lower right hand corner of the bench sheet. Include reagent lot numbers. Include the Metals Section reference number and volume used for all reagents and laboratory control samples. Original bench sheets are given to the Metals Prep Supervisor for review. A copy of the bench sheet is placed in a logbook to be kept at the bench for easy reference.

These procedures were developed specifically for use by HERITAGE LABORATORIES INC. and may not be applicable for other organizations.

HERITAGE LABORATORIES, Inc.

SOP Correction FORM

SOP Number: AM-206.0

SOP Title: SW 846, 9040, 9045 pH

Page #: 1

Requested by : Dave C Date: 1-6-94

Correction: SW 846 9040A, 9045A

Reason (if applicable): Reflect updates

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: _____ Date: _____

100892

DRAFT

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EMS Test Codes: G402.7
Method Quote: EPA 160.1 (Gravimetric, Dried at 180°C)

TOTAL DISSOLVED SOLIDS

Referenced Procedures - (USEPA Method 160.1, Standard Methods 2540-C,)

I. Introduction

This method is applicable to the determination of total dissolved solids in drinking, surface, and saline waters, domestic and industrial wastes. Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally taste bad and may induce illness when consumed. Highly mineralized waters are unsuitable for many industrial applications. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

A. Test - G402.7 (EPA 160.1)
B. Method Detection Limit - 10 mg/L
C. Containers - Plastic or glass containers
D. Preservatives - refrigeration at 4°C
E. Regulatory Holding Time - 48 hrs
F. Recommended Holding Time - 48 hrs

II. Extraction Procedures

A. Theory

Summarizing the method, a well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids.

B. Apparatus

1. Glass fiber discs 4.7cm or 2.1 cm, without organic binder
2. Filter holder, membrane filter funnel
3. Suction flask, 500 mL
4. Evaporating dishes, porcelain, 100 mL volume.
5. Drying oven, 180°C ± 2°C
6. Desiccator
7. Analytical balance

D. Procedure

1. Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus. While vacuum is applied, wash the disc with three successive 10 mL volumes of distilled water. Remove all traces of water

by continuing to apply vacuum after water has passed through. Discard washings.

2. Preparation of evaporating dishes: Heat the clean evaporating dish to 180°C ± 2°C until completely dry (3 to 4 hrs). Cool in desiccator and store until needed. Weigh immediately before use.
3. Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of a 100 mL graduated cylinder.

   NOTE: If sample will not filter through, use smaller volume.
4. Filter the sample through the glass fiber filter, rinse with three 10 mL portions of distilled water, and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.
5. Transfer 100mL (and rinsings) of the filtrate to a weighed evaporating dish and place the dish in the drying oven (180°C). Evaporate to dryness.
6. After sample has reached complete dryness, cool in a desiccator for approximately 2 hours. Weigh the dish and record weight on bench sheet. Repeat the drying cycle until a constant weight loss of less than 0.5mg is obtained.

III. Analysis Procedure

Not Applicable

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

QAQC samples are done per total dissolved solids run as follows:

Method Prep Blank (BLA02)- one per run (day)
Internal Control Verification Std (ICV02)- one per run (day)
Matrix Duplicate (DUP02)-one per every 10 samples

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

All total dissolved solids prep data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Calculate total dissolved solids as follows:

$$\text{Filterable residue, mg/L} = \frac{(A - B) \times 1{,}000}{C}$$

where:
A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in mL

VI. Interferences/Troubleshooting

Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate, may be hygroscopic and will require prolonged drying, desiccation, and rapid drying.

If there is too much residue in the evaporating dish, water can be trapped that will not evaporate during drying. Total residue should be limited to about 200 mg.

Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying to insure that all the bicarbonate is converted to carbonate.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves.

VIII. Clean Up and Disposal

All glassware should be cleaned with soap and hot water. Rinse with DI water.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 160.1.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 2540-C.

EMS Test Codes: G403.6
Method Quote: EPA 160.2 (Gravimetric, Dried at 103-105°C)

TOTAL SUSPENDED SOLIDS

Referenced Procedures - (USEPA Method 160.2, Standard Methods 2540-D.)

I. Introduction

This method is applicable to the determination of total suspended solids in drinking, surface, and saline waters, domestic and industrial wastes. Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Highly mineralized waters are unsuitable for many industrial applications. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limtitations.

A. Test - G403.6 (EPA 160.1)
B. Method Detection Limit - 1 mg/L
C. Containers - Plastic or glass containers
D. Preservatives - refrigeration at 4°C
E. Regulatory Holding Time - 7 days
F. Recommended Holding Time - 7 days

II. Extraction Procedures

A. Theory

Summarizing the method, a well-mixed sample is filtered through a weighed standard glass fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids.

B. Apparatus

1. Glass fiber discs 4.7cm or 2.1 cm, without organic binder
2. Filter holder, membrane filter funnel
3. Suction flask, 500 mL
4. Watchglass
5. Drying oven, 130 to 150°C ± 2°C
6. Desiccator
7. Analytical balance

D. Procedure

1. Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water

by continuing to apply vacuum after water has passed through. Discard washings.

2. Remove filter from filtration apparatus and transfer to a watchglass as a support. Dry filter in an oven at 103 to 105°C for at least one hour. Cool in desiccator to balance temperature and weigh. Repeat the drying cycle until a constant weight loss of less than 0.5mg is obtained.
3. Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of a 100 mL graduated cylinder.

   NOTE: If sample will not filter through, use smaller volume.
4. Filter the sample through the glass fiber filter, rinse with three [illegible] mL portions of distilled water, and continue to [illegible] vacuum for about 3 minutes after filtration [illegible] complete to remove as much water as possible.
5. Transfer the filter from the filtration apparatus to a watchglass as a support. Dry for at least 1 hour at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh. Record weight of filter on bench sheet. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight loss of less than 0.5mg is obtained.

III. Analysis Procedure

Not Applicable

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

QAQC samples are done per total suspended solids run as follows:

Method Prep Blank (BLA02)- one per run (day)
Internal Control Verification Std (ICV02)- one per run (day)
Matrix Duplicate (DUP02)-one per every 10 samples

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

All total suspended solids prep data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Calculate total suspended solids as follows:

$$\text{Non-Filterable residue, mg/L} = \frac{(A - B) \times 1{,}000}{C}$$

where:
A = weight of filter + dried residue in mg
B = weight of filter in mg, and
C = volume of sample used in mL

VI. Interferences/Troubleshooting

Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

If there is too much residue in the evaporating dish, water can be trapped that will not evaporate during drying. Total residue should be limited to about 200 mg.

For samples high in dissolved solids thoroughly wash the filter to ensure removal of the dissolved material.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves.

VIII. Clean Up and Disposal

All glassware should be cleaned with soap and hot water. Rinse with DI water.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 160.2.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 2540-D.

THIS IS AN EXACT COPY OF THE ORIGINAL DOCUMENT

EMS Test Code: G605.2
Method Quote: EPA 310.1 (Titrimetric)

CONFIDENTIAL

ALKALINITY

BY _____ DATE _____

Referenced Procedures - (USEPA Method 310.1, Standard Methods 2320-B.)

I. Introduction

This method is applicable to the determination of alkalinity of drinking, surface, and saline waters, domestic and industrial wastes. Alkalinity measures the ability of a sample to react with a standard acid to a given pH. This data is useful in wastewater treatment to interpret the efficiency of the process. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents.

A. Test - G605.2
B. Method Detection Limit - 1 mg/L
C. Containers - Plastic or glass bottles
D. Preservatives - refrigeration at 4° C
E. Regulatory Holding Time - 14 days
F. Recommended Holding Time - 14 days

II. Extraction Procedures

A. Theory

The pH of the sample is determined and then titrated with the appropriate level of standard acid (H_2SO_4) to pH 4.5.

B. Apparatus
1. pH Meter
2. Buret
3. 9 oz. Cups
4. Graduated Cylinder

C. Reagents
1. Sulfuric acid
   a. 0.02 N (pH range 4.5 - 6.5)
   b. 0.1 N (pH range 6.5 - 8.3)
   c. 1 N (pH range ≥ 8.3)
2. Sodium carbonate (dried @ 250°C 4 hrs.)

D. Procedure

No advance sample preparation is required. The samples are titrated directly.

III. Analysis Procedure

A. Theory

Basic ions in solution react with the standardized H_2SO_4 solution to a given pH. A pH of 4.5 is used as the end point for total alkalinity which includes hydroxide, carbonate, and bicarbonate as the major contributors to the alkalinity value.

B. Method

1. Standardization of Titrant
   a. Weigh 2.5g ± 0.2 of the dried sodium carbonate, transfer to a 1 liter volumetric flask, and dilute to volume.
   b. Titrate to the pH endpoint (4.5) with H_2SO_4, using 40.0 ml of sodium carbonate solution in flask.
   c. Record the amount of H_2SO_4 used to titrate with on the bench sheet and calculate normality (see calculation section).

2. Sample analysis
   a. Number the 3oz. cups with corresponding sample number.
   b. Measure 50ml of sample into each cup.
   c. Choose normality of sulfuric acid by pH of sample.
   d. Note the starting mark of the buret on the alkalinity worksheet.
   e. Slowly add H_2SO_4 until pH reaches 4.5.
   f. Record ending point as H_2SO_4 on lab sheet when endpoint is reached.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

QAQC samples are done per alkalinity run as follows:

Matrix Duplicate (DUP02)-one per every 10 samples

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

All alkalinity prep data generated is reviewed by the group

leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Calculate H_2SO_4 normality as follows:

$$\frac{A \times B}{53.00 \times C}$$

where,
A = g of sodium carbonate weighed into flask
B = ml of sodium carbonate solution used for titration
C = ml of titrant (H_2SO_4)

Calculate value of alkalinity in sample as follows:

$$\frac{\text{mls of } H_2SO_4 \text{ used} \times \text{Normality} \times 50{,}000}{\text{mls of sample used}}$$

VI. Interferences/Troubleshooting

Do not filter any samples

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. Follow ordinary laboratory practices.

VIII. Clean Up and Disposal

Samples can be disposed of down the sink with copious amounts of cold water. Plastic cups can be rinsed out with cold water and then thrown into the garbage can.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 310.1.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 2320-B.

SOP Correction FORM

SOP Number: GN-10-10.0

SOP Title: ALKALINITY

Page #: 2

Requested by : Barb Shrake Date: 10/9/92

Correction: Under QAQC:
LCS (ICV01) and the Continuing Calibration Verification Standards ~~or~~ (CCV) are prepared from different sources. The CCV is analyzed at a frequency of 10 percent in the alkalinity run.

Reason (if applicable):

Correction has been implemented (Y/N): N Date :

Correction will be implemented by (date): 11/1/92

Correction will be included in next SOP revision by (date): 4/93

APPROVAL

Laboratory Manager
Signature: [signature] Date: 10/14/92
100892

SOP Correction FORM

SOP Number: GN-[illegible]

SOP Title: ALKALINITY

Page #: 2

Requested by : CHRIS BOYLE Date: 12-3-92

Correction: UNDER DAQC:

LCS (ICVC1) - ONE PER RUN OR DAILY

Reason (if applicable):

Correction has been implemented (Y/N): Y Date : 8-25-92

Correction will be implemented by date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager Signature: [signature] Date: 12-3-92

100892

Revision Date _____ BY _____ DATE _____

EMS Test Codes: G102.9
Method Quote: EPA 325.1 (Colorimetric, Automated Ferricyanide AAI)

CHLORIDE ANALYSIS
by Lachat Quikchem AE

Referenced Procedures - (USEPA Method 325.1, Standard Methods 4500-Cl^-, 4500-Cl^- E.)

I. Introduction

This method is used to analyze chloride in drinking, surface, and saline waters, and domestic and industrial wastes. Chloride, in the form of chloride (Cl^-) ion, is one of the major inorganic anions in water and wastewater. Higher concentrations of chloride are found in wastewater than in raw water and concentrations may be increased by industrial processes. Along the sea coast, chloride is sometimes present due to leakage of salt water into the sewage system. High concentrations of chloride may be harmful to growing plants, as well as cause damage to metallic pipes and structures.

A. Test - G102.9 (Chloride, colorimetric, automated)
B. Method Detection Limit - 1.0mg/L
C. Containers - chemically resistant glass or plastic bottles
D. Preservatives - No special preservative is necessary
E. Regulatory Holding Time - 28 days
F. Recommended Holding Time - 28 days

II. Extraction Procedures

A. Theory

Summarizing the method, chloride reacts with mercuric thiocyanate to form a strong, covalent complex ($HgCl_2$) which displaces thiocyanate (SCN). The liberated SCN then reacts with aqueous iron(III) to produce the red hexacyanoferrate(III) or ferricyanide ion. This ion is then measured colorimetrically at 480 nm.

B. Apparatus
1. Automatic sampler
2. Proportioning pump
3. Injection module with a 20cm 0.8mm i.d. sample loop
4. Colorimeter
   a. interference filter: 480nm
   b. flow cell: 10mm
5. Reaction module 10-117-07-1-B (manifold)
6. Lachat QuikCalc II software system to record data
7. 13 X 100mm culture test tubes
8. Acrodisc filters - PTFE 0.45uM

C. Reagents

All reagents should be made up using Millipore deionized water.

1. Combined Color Reagent

a. Stock Mercuric Thiocyanate Solution

In a 1 L volumetric flask, dissolve 4.17g of mercuric thiocyanate ($Hg(SCN)_2$) in about 500 mL of methanol. Dilute to the mark with methanol and invert three times. **CAUTION:** Mercury is a very toxic metal. Wear gloves, and take care of any spills in the correct manner.

b. Stock Ferric Nitrate Reagent, 0.5 M

In a 1 L volumetric flask, dissolve 202g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in approximately 800 mL of water. Add 25 mL of conc. nitric acid and dilute to the mark. Invert three times.

c. Combined Color Reagent

In a 500 mL volumetric flask, mix 75 mL of stock mercuric thiocyanate solution with 75 mL of stock ferric nitrate reagent and dilute to the mark. Invert three times. Vacuum filter through a 0.45 micrometer membrane filter.

2. Stock Chloride Standard - 1000 mg Cl^-/L

Dry 2g of primary standard grade sodium chloride (NaCl) overnight. In a 1 L volumetric flask, dissolve 1.648g of primary grade sodium chloride in about 500 mL of water. Dilute to the mark and invert three times.

D. Procedure

No advance sample preparation is required. However, if samples are turbid or have any suspended solid particles they should be filtered through a 0.45 uM filter into the sample tube before analysis.

III. Analysis Procedure

A. Theory

Flow injection analysis is based on injection of a liquid sample into a moving nonsegmented carrier stream of a reagent. The injected sample forms a zone (plug) that disperses on its way to a detector. The Lachat system basically consists of a pump that propels the carrier stream, an injection valve which introduces the sample plug into the carrier stream, and sample coils in which the sample plug disperses and reacts with the components of the carrier stream (color reagent) forming a colored species to be sensed by the flow through detector (480nm). The signal being detected is seen as a peak, the height of which is related to the concentration of analyte.

Using this technique, chloride in drinking, surface, and saline waters and domestic and industrial wastewaters, can be

determined over a range of 1.0 to 100 mg Cl^-/L on the Lachat system. The range may be extended with sample dilution. Approximately 120 samples per hour can be analyzed.

B. Method

1. Instrument setup

Before turning on the Lachat system, several things need to be checked. Fill the carrier and wash reagent bottles with fresh Millipore DI water. Check the color reagent bottle to assure it is adequately filled for a run, and that it has been recently made up. If any particulate matter is seen in any reagent bottle, make up fresh reagent.

Inspect all pump tubing to make sure there are no obstructions in the lines and that none of the tubing needs to be replaced. Inspect manifolds and the 6-port injection valve for proper connections. Place reagent feedlines into proper containers and raise tension levers on pump tube cassettes.

Turn on power at the main power switch to reboot the computer, system unit, and sampler. Turn on the pump to override standby to allow reagents to pump through the system. Once all air bubbles have been pumped out of the lines, download the chloride method from the IBM computer to the system unit. Establish a stable baseline before analyzing standards or samples.

The chloride method should be set up to include the following parameters:

Pump speed - 35
Cycle period - 30s
Load period - 15s
Inject period - 15s
Gain - 149 X 1

Chloride:
Inject to start of peak period - 5s
Inject to end of peak period - 30s

2. Calibration

A set of seven working solutions are used to calibrate the chloride method.

Into seven 250ml volumetric flasks pipet, respectively,

25.00, 20.00, 15.00, 10.00, 5.00, 2.00, and 1.00 mL

of the working stock solution (Reagent 2.-1000mg Cl^-/L). Dilute to the marks with DI water and invert each three times. This makes

100, 80, 60, 40, 20, 8.0, and 4.0 mg Cl^-/L

respectively.

Place calibration standards in calibration tray in descending order of concentration. Load unknown samples into sample racks to be run following calibration. On the Lachat XYZ sampler, the sample rack will not be processed until a calibration curve has passed (corr. coeff.= .998).

3. Instrument shutdown

At the end of the run, place all feedlines into a wash DI water container. Flush the system for approximately 15-20 minutes. At the end of this time remove feedlines from the water and pump the system dry. Turn off the pump and release tension levers on pump tube cassettes. The main power switch can then be turned off.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. A start-up test of the instrument in use is done to establish the laboratory's ability to set up and operate the analytical equipment and procedures. The purpose is to prove that the analytes of interest can be detected under the parameters set forth and that the analyst can identify the analytes. This includes a detection limit determination which is performed both when a new analysis is first begun, and at timely intervals while the instrument is up and functioning. Both instrument and method detection limits are determined at this time.

To further assure the representativeness of data produced for the Lachat instrument tests, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix duplicates.

QAQC samples are done per run as follows:

Method Prep Blank (BLA01)- one per run

Laboratory Control Sample (LCS)- one per run

Matrix Spike (SPI01)- one per 20 samples-with 80-120% recovery

*NOTE- Add spiking solution with syringe to ensure accuracy.

Matrix Duplicate (DUP01)-one per 10 samples-with replicability <= 20%

Continuing Calibration Verification (CCV01)- one at beginning, one per 10 samples

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

All chloride generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Sample concentrations are computed directly from the standard calibration curve obtained at the beginning of each run (absorbance vs. Cl^- concentration). Results are reported as milligrams Cl^- per liter.

VI. Interferences/Troubleshooting

It is of the utmost importance that the water used in preparing reagents and standards be completely free of contaminants. Therefore be sure to use Millipore DI water.

Interferents belong to two classes: Substances which reduce iron(III) to iron(II) and mercury(III) to mercury(II). (e.g. sulfite, thiosulfate), and other halides which also form strong complexes with mercuric ion (e.g. Br^-, I^-).

Routine maintenance includes changing pump tubing when necessary, cleaning unions at each of the port valves, checking and replacing o-rings and flares as necessary, and silicone treating the pump rollers every 50 hours of use.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves.

Elemental mercury (Hg) used in the color reagent, in both liquid and vapor forms, is toxic due to its liquid solubility, lack of charge, and membrane permeability. Exposure to mercury vapors and absorption through the skin can be toxic and cause chest pains, pneumonitis, and coughing. Do not dipose of mercury down the drain. Collect in a tightly secured container for reclaim or disposal.

VIII. Cleanup and Disposal

Samples from tubes can be poured down the sink. Flush with copious amounts of cold water. Sample tubes can be washed and reused. Wash each three times with regular DI water, and three times with Millipore DI water.

Make sure to put lids on all reagent bottles and calibration vials when finished.

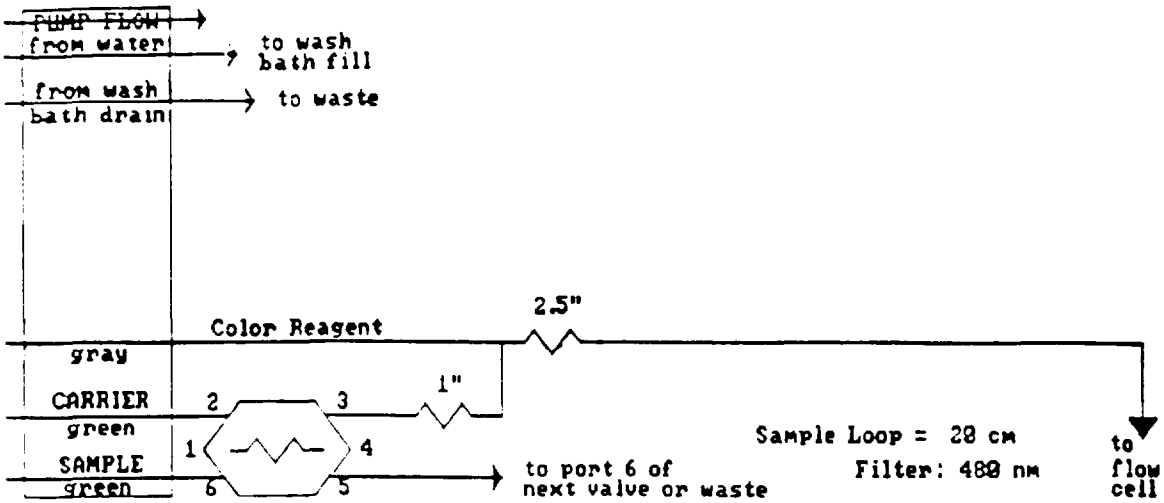
IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 325.1.

Lachat Quikchem Method No. 10-117-07-1-B

Standard Methods for the Examination of Water and Wastewater, 16th ed., 1985, Method 4500-Cl^- E.

Manifold Diagram:



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
2.5"	is	168	cm of tubing on a 2.5 in coil support
3"	is	202	cm of tubing on a 3 in coil support
4"	is	255	cm of tubing on a 4 in coil support
8"	is	550	cm of tubing on a 8 in coil support

Heated tubing is shown inside a box with the temperature next to the box. Heated tubing is **650** cm unless otherwise specified.

All manifold tubing is **0.8** mm (0.032 in) i.d. This is 5.2 uL/cm.

Notes:

MANIFOLD DIAGRAM REVISION DATE: 7 August 1986

SOP Correction FORM

SOP Number: [illegible]

SOP Title: Nitrate Analysis

Page #: 1

Requested by : Scott Anderson Date: 7-1-03

Correction: Change referenced method to USEPA Method 325.2

Reason (if applicable): Lachat Method References USEPA Method 325.2.

Correction has been implemented (Y/N): _____ Date : _____

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): _____

APPROVAL

Laboratory Manager
Signature: [illegible] Date: 7/2/03

110892

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DATE

EMS Test Codes: G102.4
Method Cuote: Standard Method 407A (Argentometric)

CHLORIDE ARGENTOMETRIC ($AgNO_3$)

Referenced Procedures - (Standard Methods 4500-Cl^-)

I. Introduction

This method is used to analyze chloride in drinking, surface, and saline waters, and domestic and industrial wastes. Chloride, in the form of chloride (Cl^-) ion, is one of the major inorganic anions in water and wastewater. Higher concentrations of chloride are found in wastewater than in raw water and concentrations may be increased by industrial processes. Along the sea coast, chloride is sometimes present due to leakage of salt water into the sewage system. High concentrations of chloride may be harmful to growing plants, as well as cause damage to metallic pipes and structures.

A. Test - G102.4 (SM- 407A)
B. Method Detection Limit - 5.0 mg/L
C. Containers - Plastic or glass bottles
D. Preservatives - refrigeration at 4°C
E. Regulatory Holding Time - 28 days
F. Recommended Holding Time - 28 days

II. Extraction Procedures

A. Theory

Summarizing the method, potassium chromate is used as an indicator to indicate the end point of the silver nitrate titration of chloride in a sample. Silver chloride is precipitated quantitatively before red silver chromate is formed.

B. Apparatus

1. Plastic cups
2. Jencons Digitrate

C. Reagents

1. Potassium chromate indicator solution

   Dissolve 50 g K_2CrO_4 in a little DI water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 hours, filter, and dilute to 1 L with distilled water.

2. Standard silver nitrate titrant - 0.0141 N

   Purchased already prepared from Red Bird Services.

3. Standard sodium chloride - 0.0140 N

   Dissolve 0.824 g NaCl (dried at 140°C) in DI water and dilute to 1000mL in a volumetric flask.

D. Procedure

No advance sample preparation is required (samples requiring the total halogen analysis are prepped using the Total Halogen SOP).

III. Analysis Procedure

A. Theory

In a neutral or slightly alkaline solution, potassium chromate ion indicates the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

B. Method

1. Standardization of $AgNO_3$ solution (Reagent 2.)
   a. Into three separate plastic cups, measure 90 mL of DI water.
   b. Add 10 mL of NaCl solution (Reagent 3.) to each cup.
   c. Add 1 mL of K_2CrO_4 indicator solution to each cup. The solution will turn yellow at this point.
   d. Fill the digitrate with $AgNO_3$ solution.
   e. Titrate the solution in the cup with $AgNO_3$ until it turns orange in color (approximately 10 mL $AgNO_3$ will be needed).
   f. Repeat the titration for the two remaining cups and record amount of $AgNO_3$ used on the bench sheet. Subtract out the value for a blank sample.

4. Analyzing samples
   a. Measure 100 mL of sample into a plastic cup. For soil samples, prepare a solution of 1 g of sample to 100 mL DI water and filter.
      NOTE: For sales samples, it is necessary to adjust the pH to between 7 and 8.
   b. Add 1 mL K_2CrO_4 indicator solution.
   c. Fill the digitrate with $AgNO_3$ solution.
   d. Titrate the solution in the cup with $AgNO_3$ until it turns orange in color.
   e. Record the amount of $AgNO_3$ used to titrate the sample on the bench sheet.

      NOTE: If more than 15 mL of $AgNO_3$ are needed to titrate a sample, the sample must be diluted.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In

addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates. The following QAQC is done for each chloride run:

Method Prep Blank (BLA01)- one per run (day)
Continuing Calibration Verification Std (CCV01) - one/10 samples
Internal Control Verification Std (ICV01)- one per run (day)
Matrix Spike (SPI01)- one per every 20 samples/ or per run
Matrix Duplicate (DUP01)-one per every 10 samples

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

Acceptable recovery range for QAQC standards (CCV, ICV, LCS) is 90-110%. Recovery range for spikes is 80-120%.

All chloride data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Normality of $AgNO_3$ is calculated as follows:

$$mL\ NaCl \times Normality\ NaCl \times \frac{1}{mL\ AgNO_3} = N$$

Calculate chloride values as follows:

$$mg\ Cl^-/L = \frac{(A - B) \times 35{,}450 \times N}{vol.\ sample\ (mL)}$$

where:
A = mL $AgNO_3$ used to titrate sample
B = mL $AgNO_3$ used to titrate blank
N = normality of $AgNO_3$ solution

Multiply the result (as well as the detection limit) by any dilution factors. For soil samples (1g to 100 mL) the result must be multiplied by 100 for the 1:100 dilution.

VI. Interferences/Troubleshooting

Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with hydrogen peroxide. Iron in excess of 10 mg/L interferes by masking the end point. Orthophosphate in excess of 25 mg/L interferes by precipitating as silver phosphate.

For best results of this test, be consistent in end point recognition.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves.

VIII. Clean Up and Disposal

Samples may be disposed of down the sink with water. Plastic cups may be discarded into the trash.

IX. References

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 4500-Cl^-.

Annual Book of ASTM Standards, Method D-808TX.

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DATE _____

EMS Test Codes: P203.4
Method Quote: EPA 350.2 (Colorimetric: Titrimetric: Potentiometric - Distillation Procedure)

AMMONIA NITROGEN DISTILLATION

Referenced Procedures - (USEPA Method 350.2, Standard Methods 4500)

I. Introduction

This distillation method is applicable to the determination of ammonia-nitrogen in drinking, surface, and saline waters, domestic and industrial wastes. In general, direct manual determination of low concentrations of ammonia is confined to clean water samples and good-quality nitrified wastewater effluent. In other instances, and where interferences are present and greater precision is necessary, a preliminary distillation step is required.

A. Test - P203.4 (EPA 350.2)
B. Method Detection Limit - 0.1 mg/L (mg/kg for soils)
C. Containers - Plastic or glass bottles
D. Preservatives - 2 mL Sulfuric acid per liter and refrigeration at 4°C
E. Regulatory Holding Time - 28 days
F. Recommended Holding Time - 28 days

II. Extraction Procedures

A. Theory

Summarizing the method, the sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds. It is then distilled into a solution of H_2SO_4. The ammonia in the distillate is then determined using the ammonia electrode method.

B. Apparatus

1. Distillation apparatus including a 1000 mL round-bottomed flask, connecting arm, West condenser, and a 500 mL Erlenmeyer flask (collecting vessel).
2. Heating mantle - adjustable
3. Boiling beads
4. Graduated cylinder
5. pH paper

C. Reagents

1. Millipore DI water (ammonia-free).
   All reagents are to be made up with this water.
2. Sodium hydroxide solution 10N
   Purchased already prepared from Red Bird Service.
3. Borate buffer solution
   Purchased already prepared from Red Bird Service.

4. Sulfuric acid (H_2SO_4) - .1 N
   Add 50 ml 1 N H_2SO_4 to 400 mL DI water in a 500 mL volumetric flask. Dilute to the mark and mix.
5. Ammonium chloride standard solution (stock) - 1000 mg/L

D. Procedure

1. To prepare the extraction equipment add 500 mL water and a few boiling beads to a distillation flask and steam out the distillation apparatus. This will get rid of any residual traces of ammonia present in the glassware.
   NOTE: To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation.
2. Using a graduated cylinder, measure 200 mL of sample (2.5g to 250 mL DI for soils) into a 1000 mL boiling flask.
3. Add 25 mL borate buffer solution to the boiling flask.
4. Adjust pH to 9.5 with 10 N NaOH (check with pH paper).
5. Add boiling beads to the distillation flask.
6. Close the distillation system making sure to turn on the water to the condenser.
7. Add 25 mL 0.1 N H_2SO_4 to the 500 mL receiving Erlenmeyer flask. Make sure that the dripper (teflon tube) is below the surface of the solution.
8. Turn on the heating mantle to begin distillation. Continue the distillation until approximately 150 mL of distillat has been collected.
9. Dilute the sample distillate to 250 mL (total) with DI water and transfer to a sample bottle for later analysis.

III. Analysis Procedure

Not Applicable

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

QAQC samples are done per ammonia distillation run as follows:

Method Prep Blank (BLA02)- one per run (day)
Matrix Spike (SPI02)- one per every 20 samples/ or per run
Matrix Duplicate (DUP02)-one per every 10 samples/ or per run

All ammonia distillation prep data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for makir sure that all relevant information has been recorded correctly a. that all QAQC has been completed. No one can review their owi.

data. Each run sheet is initialled and dated by the reviewer.

V. Calculations
Not Applicable

VI. Interferences/Troubleshooting

Glycine, urea, glutamic acid, cyanates, and acetamide hydrolyze very slowly in solution on standing but, of these, only urea and cyanates will hydrolyze on distillation at pH of 9.5.

Residual chlorine should be removed before distillation.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. Sulfuric acid used in the prep is corrosive.

Ammonia is not a "poison", however its alkalinity is corrosive to body tissues. Prolonged or repeated skin contact can cause serious damage or burns.

VIII. Clean Up and Disposal

All glassware should be cleaned with soap and hot water. Rinse with DI water. Reaction vessel waste may be disposed of down the sink with water.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 350.2.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 4500.

SOP Correction FORM

SOP Number: GN-10-22.0

SOP Title: Ammonia Nitrogen Distillation

Page #: 2

Requested by : Barb Shrake Date: 10/13/92

Correction: Under D. Procedure . . . #3. Should read: Adjust pH to 9.5 with 10N NaOH using pH meter. #4 Should read: Add 25 ml borate buffer solution to the boiling flask.

Reason (if applicable):

Correction has been implemented (Y/N): Y Date : 10/12/92

Correction will be implemented by (date):

Correction will be included in next SOP revision by (date):

APPROVAL

Laboratory Manager Signature: Gary A. Klingler Date: 10/27/92

100892

SOP Correction FORM

SOP Number: GN-10-22.0

SOP Title: Ammonia Nitrogen Distillation

Page #: 2

Requested by : Barb Shrake Date: 10/27/92

Correction: Under D. Procedure . . . #7. Should read Add 25mL 2% boric acid to the 500mL receiving Erlenmeyer flask . . .

Reason (if applicable): _____

Correction has been implemented (Y/N): Y Date : 10/26/92

Correction will be implemented by (date): _____

Correction will be included in next SOP revision by (date): 4/93

APPROVAL

Laboratory Manager
Signature: [signature] Date: 10/28/92
100892

IS AN EXACT COPY OF
ORIGINAL DOCUMENT.

DATE

EMS Test Codes: G203.2, G203.4, G203.5
Method Quote: EPA 350.3 (Potentiometric, Ion Selective Electrode)

NITROGEN, AMMONIA

Referenced Procedures - (USEPA Method 350.3, Standard Methods 4500)

I. Introduction

This distillation method is applicable to the determination of ammonia-nitrogen in drinking, surface, and saline waters, domestic and industrial wastes. Ammonia is present naturally in surface and wastewaters. Its concentration generally is low in groundwaters because it adsorbs to soil particles and clays and is not leached readily from soils. It is produced largely by deamination of organic nitrogen-containing compounds and by hydrolysis of urea.

A. Test - P203.4 (EPA 350.3)
B. Method Detection Limit - 0.1 mg/L (mg/kg for soils)
C. Containers - Plastic or glass bottles
D. Preservatives - 2 mL Sulfuric acid per liter and refrigeration at 4°C
E. Regulatory Holding Time - 28 days
F. Recommended Holding Time - 28 days

II. Extraction Procedures

A. Theory

Summarizing the method, the ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale.

B. Apparatus

1. Electrometer with expanded mV scale (set to relative mV)
2. Ammonia selective-electrode
3. Probe stand
4. Stir plate and stir bar
5. Graduated cylinder
6. Plastic cups

C. Reagents

1. DI water (ammonia-free).
   All reagents are to be made up with this water.
2. Sodium hydroxide solution 10N
   Purchased already prepared from Red Bird Service.
3. Ammonium chloride stock standard solution - 1000 mg/L
   Dissolve 3.819g ammonium chloride (NH_4Cl) in water and bring to volume with DI water in a 1 L volumetric flask.

D. Procedure

A majority of the samples must be distilled before analysis can be performed (see ammonia distillation sop). No sample prep is necessary if the sample does not require distillation.

III. Analysis Procedure

A. Theory

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

B. Method

1. Ammonia probe set up
   a. Rinse the probe with DI water.
   b. Place 15 drops of ammonia electrode internal filling solution into the ammonia probe cap. Making sure there are no air bubbles trapped, screw the cap onto the end of the probe.
   c. Place the probe into a solution of pH 4 buffer for 15 minutes.
2. Instrument calibration
   a. Prepare the following levels of calibration standards in order to calibrate the meter (use DI water to bring standards up to volume):

      10ppm - 10 mL of NH_4Cl stock (Reagent 3.-1000 mg/L) to final volume of 1 L.
      1ppm - 100 mL of 10ppm std to final volume of 1 L.
      .1ppm - 100 mL of 1ppm std to final volume of 1 L.
      5ppm - 25 mL of 10ppm std to final volume of 50 mL.
      .5ppm - 25 mL of 1ppm std to final volume of 50 mL.

   b. Calibrate the meter by using the 10ppm standard to zero the mV reading (adjust by turning the calibration knob). Read the 10ppm standard until the mV reading remains stable at zero (if the zero reading does not remain stable through the run, the meter must be recalibrated).
   c. Calibration standards are treated the same as samples when being read. Measure 50 mL of standard into a plastic cup, add a magnetic stir bar, and place cup on a stir plate. Just prior to reading the standard, add 10 N NaOH solution dropwise to the cup until the mV reading just starts to drop. From this point, time the reaction for 2 minutes and record the final

mV reading. After each standard and sample has been read, rinse the probe with DI water, place in pH 4 buffer solution, and wait until the meter reads 130 mV before running the next sample.

d. Run the five levels of calibration standards and record each mV reading.

e. Run samples only after a calibration curve has passed (correlation coefficient 2.9980).

NOTE: All samples which read 10 mV or less on the meter must be diluted into range.

f. At the end of analyses, rinse the probe and remove the cap for storage. Place the probe in a solution of pH 7 buffer until the next run.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. A start-up test of the instrument in use is done to establish the laboratory's ability to set up and operate the analytical equipment and procedures. The purpose is to prove that the analytes of interest can be detected under the parameters set forth and that the analyst can identify the analytes. This includes a detection limit determination which is performed both when a new analysis is first begun, and at timely intervals while the instrument is up and functioning. Both instrument and method detection limits are determined at this time.

To further assure the representativeness of data produced, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix duplicates.

For ammonia nitrogen runs where samples have been prepped via ammonia distillation the following QAQC is performed:

Method Prep Blank (BLA02)- one per run (day), must be ≤.10mg/L
Matrix Spike (SPI02)- one per every 20 samples/ or per run
Continuing Calibration Verification (CCV01) - one per 10 samples
Matrix Duplicate (DUP02)-one per 10 samples-with replicability ≤ 20%
Internal Control Verification Std. (ICV02) - 1.0 ppm/ one per run.

For ammonia nitrogen samples run where distillation is not done, the following QAQC is performed:

Method Prep Blank (BLA01) - one per run, must be ≤.10mg/L
Continuing Calibration Verification Std (CCV01)- one per 10 samples
Internal Control Verification Std. (ICV01) - EPA source/ one per run.

Matrix Spike (SPI01)- one per 20 samples
Matrix Duplicate (DUP01)-one per 10 samples-with replicability 20%

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

Acceptable recovery range for QAQC standards (CCV, ICV, LCS) and spikes is 80-120%.

All ammonia nitrogen data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Prepare a standard curve by entering concentration values (x-axis) vs. mV reading (y-axis) into the TI-60 or TI-55 calculator. The following sequence of keys is used to prepare the curve:

1. conc. of std (mg/L)
2. [x*y]
3. mV reading
4. [Σ+]
5. Repeat steps 1-4 for all five standards
6. [2nd][Corr] calculates correlation coefficient
7. [2nd][Slope] calculates slope of curve
8. [2nd][Intcp] calculates intercept of curve

Record the correlation coefficient, slope, and intercept on the calculation sheet for documentation purposes. The correlation coefficient must be ≥0.998 for acceptance.

To calculate sample concentrations enter the sample mV reading into the standard curve [2nd][x^{1}]. This will give the concentration of the sample in mg/L (mg/kg for soils). Multiply the result (as well as the detection limit) by any dilution factors (including the distillation prep factor of 200/250 for samples which have been distilled). For soil samples (2.5g to 250 mLs) the result must be multiplied by 100 for the 1:100 dilution.

VI. Interferences/Troubleshooting

Most known interferences are eliminated or reduced to a minimum by distillation.

Volatile amines act as a positive interference.

Mercury interferes by forming a strong complex with ammonia. Do not preserve samples with mercuric chloride.

If ammonia probe does not remain stable during the run, check for trapped air bubbles on the cap membrane. If bubbles cannot be eliminated, replace the cap with a new one.

If probe acts sluggish, fill the cap with new filling solution or rinse with hot water.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. Sulfuric acid used in the prep is corrosive.

Ammonia is not a "poison", however its alkalinity is corrosive to body tissues. Prolonged or repeated skin contact can cause serious damage or burns.

VIII. Clean Up and Disposal

All glassware should be cleaned with soap and hot water. Rinse with DI water. Sample waste may be disposed of down the sink with water. Sample cups may be discarded into the garbage can.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 350.3.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 4500.

THIS IS AN EXACT COPY OF THE ORIGINAL DOCUMENT.

Revision Date _____

EMS Test Codes: G106.3, G107.3, G113.3
Method Guote: EPA 353.2 (Colorimetric, Automated, Cadmium Reduction)

NITROGEN, NITRATE-NITRITE ANALYSIS
by Lachat Quikchem AE

Referenced Procedures - (USEPA Method 353.2, Standard Methods 4500-NO_2^-B, 4500-NO_3^-F)

I. Introduction

This method is used to analyze nitrite singly, or nitrite and nitrate combined in surface and saline waters and domestic and industrial wastes. Nitrate and nitrite are two of the forms of oxidized nitrogen found in waters and wastewaters which are of greatest environmental interest. Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen.

Nitrate is found in highest amounts in the effluent of nitrifying biological treatment plants in concentrations of up to 30 mg/L . It generally occurs in trace quantities in surface and freshwater.

Nitrite is the intermediate oxidation state of nitrogen in the reduction of nitrate. This oxidation and reduction occurs in natural waters but is mainly found in wastewater treatment plants and water distribution systems. In the form of nitrous acid, nitrite can react with secondary amines to form nitrosamines, many of which are known to be carcinogens.

The LACHAT AE autoanalyzer is used to analyze nitrate-nitrite values. There is a separate manifold for nitrite (without the cadmium column) and the nitrate. In order to determine nitrate levels, the nitrite value alone is subtracted from the total (nitrate-nitrite).

A. Test - G106.3 (Nitrogen-Nitrate)
G107.3 (Nitrogen-Nitrite)
G113.3 (Nitrogen-Nitrate/Nitrite combined)
B. Method Detection Limit - .01mg/L
C. Containers - cubetainers, plastic bottles, glass containers
D. Preservatives - if run within 24 hrs.- refrigeration
if >24hrs.- conc H_2SO_4 (2ml/L) and refrig.
*Note: Samples must not be preserved with mercuric chloride or thiosulfate since this will degrade the column.
E. Regulatory Holding Time - unpreserved- 48 hrs.
preserved - 48 hrs. for NO_3^- or NO_2^- singly
28 days combined

F. Recommended Holding Time - same as above

II. Extraction Procedures

A. Theory

Summarizing the method, nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is measured colorimetrically at 520 nm. Nitrite values are measured on a separate manifold which does not include the cadmium column.

B. Apparatus

1. Automatic sampler
2. Proportioning pump
3. Injection module with a 120cm 0.8mm i.d. sample loop
4. Colorimeter
   a. interference filter: 520nm
   b. flow cell: 10mm, 1mm (optical dilutions)
5. Reaction module 10-107-04-1-B with Cd column (manifold)
6. Lachat QuikCalc II software system to record data
7. 13 X 100mm culture test tubes
8. Acrodisc filters - PTFE 0.45uM

C. Reagents

1. Nitrate-free Millipore deionized water (make up all solutions using this water)
2. Sodium hydroxide pellets
3. Ammonium chloride buffer, pH = 8.5

   In a 1L volumetric flask, dissolve 85.0g ammonium chloride (NH_4Cl) and 1.0g disodium ethylenediamine tetracetic acid dihydrate ($Na_2EDTA - 2H_2O$) in approximately 800ml DI water. Shake or stir until dissolved. Adjust pH to 8.5 with sodium hydroxide pellets and dilute to mark.
4. Sulfanilamide color reagent

   To a 1L volumetric flask add approximately 600ml Di water. Add 100ml of 85% phosphoric acid (H_3PO_4), 40.0g sulfanilamide, and 1.0g N-(1-naphthyl) ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 20min. Dilute to the mark, and invert three times. Store in a dark bottle. This solution is stable for one month.
5. Cadmium

   Place 10-20g of coarse cadmium granules in a 250ml beaker. Wash with three separate 50ml portions of dilute 6N HCl. Between each HCl wash rinse the granules thoroughly with DI water. The cadmium at this point should be silver.

CAUTION: Collect and store all waste cadmium. It is very toxic and also carcinogenic.

5. Copperized Cadmium

Prepare a 2% copper sulfate solution (20g $CuSO_4$-$5H_2O$ per liter of water) and add a 100ml portion to the cadmium prepared in 5. above. Swirl the solution for five minutes or until blue color partially fades, decant and rinse thoroughly with DI. Repeat the copper sulfate rinses two additional times rinsing with DI between each wash. The cadmium should be black or dark gray. Wash granules with at least five portions of ammonium chloride solution to remove colloidal copper. The copperized cadmium granules may be stored in a stoppered bottle under ammonium chloride solution.

7. Stock Nitrate Standard-1000 mg N/L

In a 1L volumetric flask dissolve 7.22g potassium nitrate (KNO_3)in approximately 800 mL DI water. Dilute to the mark and invert three times. Refrigerate.

8. Stock Nitrite Standard-1000 mg N/L

In a 1L volumetric flask dissolve 6.07g of potassium nitrite (KNO_2) in approximately 800 mL DI water. Dilute to the mark and invert three times. Refrigerate.

D. Procedure

1. Preparation of reduction column

The reduction column is an 8 by 50mm glass tube with the ends reduced in diameter to permit insertion into the system (Lachat part no. 5000-230). Wear gloves and do all cadmium transfers in a fume hood. Clamp the empty column upright so that your hands are free. Unscrew one of the colored fittings from an end of the column, and pull out and save the foam plug. The column and its threads are glass so be careful not to break or chip them. Fasten this fitting up higher than the open end of the column and completely fill the column, attached fittings, and tubing with ammonium chloride buffer. Scoop up copperized cadmium granules prepared in 6. above with a spatula and pour them into the top of the buffer-filled column so that they float down to the bottom of the column. Continue pouring the cadmium in and tapping the column to dislodge any air bubbles and to prevent gaps in the cadmium filling. When the cadmium granules reach to about 5mm from the open end of the column, push in the foam plug and screw on the top fitting. Rinse the outside of the column with water.

*NOTE: If air remains in the column or is introduced accidentally, connect the column into the manifold, turn the pump on maximum, and tap firmly working up the column until all air is removed.

2. Sample preparation

Because of the buffer used in this method, samples

preserved with sulfuric acid do not have to be neutralized before determination. However, if samples are over acidified (pH<1) problems with negative peaks may occur. In this case, adjust pH to between 7 and 9 with dilute NaOH.

Since nitrate-nitrogen is found in a soluble state, samples are pre-filtered through a 45uM disc filter into sample tubes prior to analysis. This eliminates turbidity and problems with restricted flow in the column due to sample particles.

III. Analysis Procedure

A. Theory

Flow injection analysis is based on injection of a liquid sample into a moving nonsegmented carrier stream of a reagent. The injected sample forms a zone (plug) that disperses on its way to a detector. The Lachat system basically consists of a pump that propels the carrier stream, an injection valve which introduces the sample plug into the carrier stream, and sample coils in which the sample plug disperses and reacts with the components of the carrier stream (buffer, color reagent) forming a colored species to be sensed by the flow through detector (520nm). The signal being detected is seen as a peak, the height of which is related to the concentration of analyte.

Using this technique, nitrate and nitrite, singly or together in potable, surface, and saline waters and domestic and industrial wastewaters, can be determined over a range of 0.01 to 0.1 mg/L on the Lachat system. The range may be extended with sample dilution.

B. Method

1. Instrument setup

Before turning on the Lachat system, several things need to be checked. Fill the carrier and wash reagent bottles with fresh Millipore DI water. Check both the buffer solution and the color reagent bottles to assure they are adequately filled for a run, and that they have been recently made up. If any particulate matter is seen in either bottle, make up fresh reagent.

Inspect all pump tubing to make sure there are no obstructions in the lines and that none of the tubing needs to be replaced. Inspect manifolds and the 6-port injection valve for proper connections. Place reagent feedlines into proper containers and raise tension levers on pump tube cassettes.

Turn on power at the main power switch to reboot the computer, system unit, and sampler. Turn on the pump to override standby to allow reagents to pump through the system. Once all air bubbles have been pumped out of the lines, stop the pump and place reduction column in the

manifold. Download the Nitrate/Nitrite method from the IBM computer to the system unit. Start the pump and allow buffer to flow through the column for approximately 5-10 minutes. Establish a stable baseline before analyzing standards or samples.

The nitrate/nitrite method should be set up to include the following parameters:

Pump speed - 35
Cycle period - 70s
Load period - 30s
Inject period - 30s
Gain - 300 x 10

Nitrate + Nitrite:
Inject to start of peak period - 24s
Inject to end of peak period - 78s

Nitrite (no column):
Inject to start of peak period - 18s
Inject to end of peak period - 72s

2. Calibration

A set of five working solutions are used to calibrate the nitrate/nitrite method. To prepare these solutions first make up a working stock solution (1.0 mg N/L) by pipeting 1.0mL stock nitrate solution (Reagent 7.) and 1.0mL stock nitrite solution (Reagent 3.) into a 1L volumetric flask. Dilute to the mark with DI water and invert three times.

Into five 250ml volumetric flasks pipet, respectively,

25.00, 20.00, 10.00, 5.00, and 2.00 mL

of the working stock solution (1.0mg/L). Dilute to the marks with DI water and invert each three times. This makes

0.100, 0.080, 0.040, 0.020, and 0.008 mg N/L

respectively.

***NOTE**: standard values for the nitrate channel will actually be doubled since both the nitrite and nitrate in the solutions will be being measured by the detector. This makes the values of the nitrate standards 0.200, 0.160, 0.080, 0.040, and 0.016 mg N/L respectively.

Place calibration standards in calibration tray in descending order of concentration. Load unknown samples into sample racks to be run following calibration. On the Lachat AZ sampler, the sample rack will not be processed until a calibration curve has passed (corr. coeff.= .998).

I. Instrument shutdown

At the end of the run, turn off the pump and remove the reduction column from manifold connecting its ends with a union fitting. Be careful not to introduce air bubbles into the column. Turn on the pump and place all feedlines into a wash DI water container. Flush the system for approximately 15-20 minutes. At the end of this time remove feedlines from the water and pump the system dry. Turn off the pump and release tension levers on pump tube cassettes. The main power switch can then be turned off.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. A start-up test of the instrument in use is done to establish the laboratory's ability to set up and operate the analytical equipment and procedures. The purpose is to prove that the analytes of interest can be detected under the parameters set forth and that the analyst can identify the analytes. This includes a detection limit determination which is performed both when a new analysis is first begun, and at timely intervals while the instrument is up and functioning. Both instrument and method detection limits are determined at this time.

To further assure the representativeness of data produced for the Lachat instrument tests, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix duplicates.

QAQC samples are done per run as follows:

Method Prep Blank (BLA01)- one per run, recovery ≤.01 (DL)

Internal Control Verication (ICV01)- two per run with 80-120% recovery

Matrix Spike (SPI01)- one per 20 samples-with 80-120% recovery

*NOTE- Add spiking solution with syringe to ensure accuracy.

Matrix Duplicate (DUP01) - one per 10 samples-with replicability ≤ 20%

Continuing Calibration Verification (CCV01) - one at beginning, one per 10 samples, recovery 80-120%

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{2|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

All nitrate/nitrite data generated is reviewed by the group leader or section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. Calculations

Sample concentrations are computed directly from the standard calibration curve obtained at the beginning of each run (absorbance vs. NO_3^--N concentration). Results are reported as milligrams oxidized N per liter (sum of NO_3^--N plus NO_2^--N) unless the concentration of NO_2^--N is separately determined and subtracted.

VI. Interferences/Troubleshooting

Build up of suspended material in the reduction column will restrict sample flow. Since nitrate/nitrogen is found in a soluble state, the sample may be pre-filtered.

Negative peaks may occur when samples have been over acidified. If this occurs, adjust the pH to between 7-9 and rerun.

Low results might be obtained for samples that contain high concentrations of iron, copper, or other metals. EDTA is added to the samples to eliminate this interference.

Take caution to filter (or extract with an organic solvent) samples that contain large concentrations of oil and grease since it will coat the surface of the cadmium, as well as the internal walls of the tubing.

Nitrite will be oxidized by O_2 quite readily. Even more of a problem is that nitric acid is absorbed from the laboratory air in a matter of a few hours. Recent findings have indicated that nonpreserved samples are stable longer than the preserved samples. For this reason, keep samples covered and cold as long as possible. Do not let racks of samples (in tubes) to be run sit out for long periods of time. Keep calibration standard vials covered when not in use.

It is of the utmost importance that the water used in preparing reagents and standards be completely free of contaminants. Therefore be sure to use Millipore DI water.

Routine maintenance includes changing pump tubing when

necessary, cleaning unions at each of the port valves, checking and replacing o-rings and flares as necessary, and silicone treating the pump rollers every 50 hours of use.

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. The reagents used in the test are of low toxicity, however, contact with acid, buffer solution, and samples themselves can cause skin damage, dryness, or burning. As mentioned before, cadmium is extremely toxic as well as carcinogenic. Exposures to cadmium dust/fume can result in pulmonary irritation, dermatitis, or allergic sensitization. Use gloves and dispose of all waste cadmium properly.

VIII. Cleanup and Disposal

Samples from tubes can be poured down the sink. Flush with copious amounts of cold water. Sample tubes can be washed and reused. Wash each three times with regular DI water, and three times with Millipore DI water.

Make sure to put lids on all reagent bottles and calibration vials when finished.

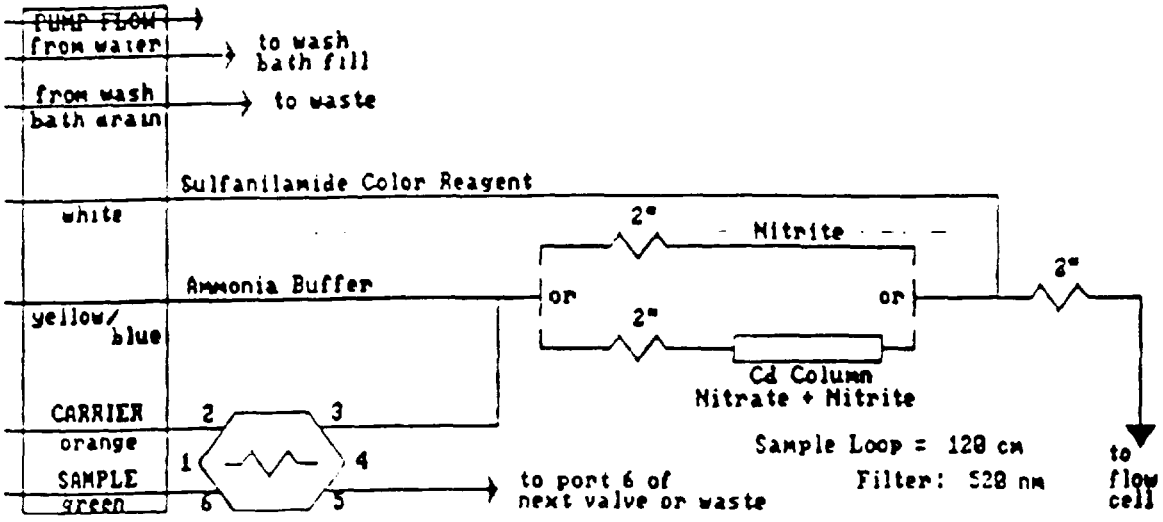
IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 353.2.

Lachat Quikchem Method No. 10-107-04-1-B

Standard Methods for the Examination of Water and Wastewater, 15th ed., 1985, Method 4500-NO_3^--E.

Manifold Diagram:



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
2.5"	is	168	cm of tubing on a 2.5 in coil support
3"	is	202	cm of tubing on a 3 in coil support
4"	is	255	cm of tubing on a 4 in coil support
8"	is	550	cm of tubing on a 8 in coil support

Heated tubing is shown inside a box with the temperature next to the box. Heated tubing is **650** cm unless otherwise specified.

All manifold tubing is **0.8** mm (0.032 in) i.d. This is 5.2 uL/cm.

Notes: A new manifold includes two packed cadmium columns.

MANIFOLD DIAGRAM REVISION DATE: 17 December 1986

EMS Test Code: G108.5
Referenced Methods:
SW846 9038
EPA 375.4
Standard Method 426C

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BY _____ DATE _____

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SULFATE TURBIDIMETRIC

I. INTRODUCTION

Sulfate is common in nature at varying concentrations. Sulfate enters the natural waters through leaching soils high in sulfate. Sulfate is also monitored in industrial discharges. Binding of the Sulfate to either Sodium or Magnesium (Glauber or Epson salt) will produce a cathartic effect. Concentrations of either mineral significantly influences the laxative effect of the Sulfate.

Holding Time	28 days
Preservative	Cool 4 degrees Celsius
Regulatory Limits	None
Detection Limits	5mg/l

II. APPARATUS AND REAGENTS

A. Hach Turbidimeter

B. Disposable Cups

C. $BaCl_2$ may purchase prepackaged HACH Sulfaver 4

D. Conditioning Reagent

Preparation: Combine in a 500ml volumetric flask:

30ml conc. HCl
100ml ethanol or isopropanol
50ml glycerol
75g NaCl and bring to mark.

3. Reagents

a. Conditioning reagent: Mix 50 mL glycerol with a solution containing 30 mL conc HCl, 300 mL distilled water, 100 mL 95% ethyl or isopropyl alcohol, and 75 g NaCl.

E. Sulfate Stock 1ml - 1000ug SO_4^{2-} = 1000ppm

Preparation: Analytically weigh 1.479g Na_2SO_4 in a liter volumetric and bring to mark.

F. EPA Mineral Standard

III. PROCEDURE

A. Theory

When $BaCl_2$ is added to a solution containing SO_4, they react to form $BaSO_4$ precipitate. The light absorbance of the $BaSO_4$ suspension can be measured, and then the concentration of SO_4 determined by comparison with a standard curve. Suspended matter and color may interfere. Correct by running blanks from which the barium chloride has been omitted.

B. Method

1. Allow samples to warm to room temperature.

2. Prepare a calibration curve using the following points and a volume of 25mls
   0 5 10 20 25 30ppm and PER at 15ppm if c.c. is between .995 and 1.0 proceed, if not check stock.

3. Place 25mls of sample into plastic cup. If a solid sample, weigh a known amount and dilute to a known volume. Take 25mls of this and analyze.

4. As the sample continues to stir, add 1 HACH Sulfaver 4 powder pillow. Allow to stir exactly one minute.

5. Add 1.00ml of the conditioning reagent and stir.

6. According to EPA, read the absorbance every 30 seconds for 4 minutes recording the highest absorbance. This would entail five minutes per sample. It has been found that the highest absorbance is around four minutes. Therefore, after the one minute of constant stirring, allow sample to sit four minutes and read the absorbance promptly at the fourth minute because consistency between samples and standards is of the utmost importance.

7. Record turbidity and construct curve.

IV. QUALITY CONTROL

Calibration Standards:	Minimum of 5 standards should be used to generate a standard curve
Linear Range:	0-30 mg/l
PER01	1 in 10 samples
DUP01	1 in 10 samples
SPI01	1 in 20 samples
BLA01	1 in 10 samples followed by a VER01
VER01	1 in 20 samples

V. CALCULATIONS

The equation below assumes all samples and standards are prepared in an identical manner.

$$\text{mg/l of } SO_4 2- = (A) \times (B)$$

A = Concentration from curve

B = Dilution factor, if any

VI. TROUBLESHOOTING/INTERFERENCES

A highly colored or turbid sample can give a false positive. A color blank should be subtracted out if necessary. Solids may be done but often creates a sample too turbid to analyze. Silica in concentrations greater than 500mg/l will also interfere.

VII. SAFETY

Follow good laboratory practice.

VIII. CLEAN UP AND DISPOSAL

Waste from this analysis may be flushed down the drain with water. Wash all reusable glassware with soap and water then DI rinse. Discard all disposable material.

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Revision Date _____ DATE _____

EMS Test Code: G801.4
Method Quote: EPA 405.1 Biochemical Oxygen Demand

CONFIDENTIAL

BIOCHEMICAL OXYGEN DEMAND ANALYSIS

Referenced Procedures - (USEPA Method 405.1, Standard Methods 5210 B.)

I. Introduction

The biochemical oxygen demand (BOD) test is used to measure the quantity of oxygen utilized by suitable aquatic microorganisms in municipal and industrial wastewaters. The BOD test measures two types of oxygen utilization: carbonaceous demand, which includes both degradation of organic material and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron ; and the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand). Measurement of carbonaceous demand only is accomplished by adding an inhibitor which stops the oxidation of nitrogen compounds.

Applications of the test to organic waste discharges allows calculation of the effect of the waste discharges on the oxygen resources of the receiving water. Data obtained from the test allows scientists and engineers to design wastewater treatment plants.

Since such conditions as temperature, water movement, sunlight, amount of microbes, etc., cannot be reproduced in the lab, a set of standard conditions has been developed so that BOD test results are comparable between labs. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

A. Test - G801.4
B. Method Detection Limit - 1.0 mg/L
C. Containers - cubetainers
D. Preservatives - refrigeration (4 degrees C)
E. Regulatory Holding Time - 24 hrs.
F. Recommended Holding Time - 6 to 24 hrs.

II. Extraction Procedures

A. Theory

Summarizing the method, samples are placed in airtight bottles and incubated for 5 days at 20 degrees Celsius in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

B. Apparatus

1. Incubation bottles - 300 mL capacity with ground glass stoppers

2. 50 mL buret
3. 500 mL Erlenmeyer flask
4. Water bath - temperature controlled at 20 degrees Celsius
5. Dissolved oxygen (DO) meter with probe

C. Reagents
1. 1N H_2SO_4 - Dilute 28 mL conc. H_2SO_4 to 1000 mL H_2O
2. 1N NaOH - Dissolve 40g NaOH in distilled H_2O, dilute to 1000mL
3. Dilution Water
   This is prepared by adding 20 mLs of each of the below solutions to 5 gallons of deionized bottled water. These solutions are purchased (already made up) from Red Bird Service.
   a. Calcium Chloride Solution - 2.75%
   b. Ferric Chloride Solution - 0.025%
   c. Magnesium Sulfate Solution - 2.25%
   d. Phosphate Buffer Solution - pH=7.2
4. Glucose-Glutamic Acid Solution (High Standard)
   Dry reagent grade glucose and reagent grade glutamic acid at 103 degrees Celsius for at least one hour. Cool and store in a desiccator. Add 150mg of each to a 1000 mL volumetric flask and dilute to volume with DI water. Dissolve the reagents by placing the flask on a magnetic stirrer. Prepare fresh daily.
5. Glucose-Glutamic Acid Solution (Low Standard)
   Dilute 50 mL "high standard" to 500mL with dilution water. Prepare fresh daily.
6. Sulfuric Acid (1+50) - Add 2mL conc H_2SO_4 to 100 mL DI water
7. Starch Solution
   Prepare a slurry of about 20g of starch in 50 mL of cold DI water. Add the slurry to about 1 L of hot DI water and stir with a glass rod. Add 0.2g salicylic acid to preserve. Cool before using.
8. Manganous Sulfate Solution
   Dissolve 480g $MnSO_4$-$4H_2O$ or 400g $MnSO_4$-$2H_2O$ or 364g $MnSO_4$-H_2O in DI water, filter and dilute to 1000 mL. Pay careful attention to the amount of water present as water of hydration (i.e., H_2O, $2H_2O$, or $4H_2O$).
9. Alkaline-Iodide-Azide Reagent
   Dissolve 10g NaN_3 into 500 mL DI water and then slowly add 480g of NaOH while stirring. Continuing to stir, add 750g NaI. Be sure that everything dissolves. (**CAUTION: This solution will become very hot when the NaOH is added**).
10. Standard Phenyarsine Oxide (PAO) Titrant- 0.0375 N
    Purchased already prepared from Red Bird Service.
11. Seed Solution
    In a 500 mL volumetric flask dissolve one capsule of BOD seed inoculum (Polyseed) in DI water. Dilute to mark and place flask on a magnetic stirrer for at least on hour.

12. Nitrification Inhibitor Solution

In a 500 mL volumetric flask dissolve one capsule of CBOD seed inoculum (Polyseed-NX) in DI water. Dilute to mark and place flask on a magnetic stirrer for at least one hour.

D. Procedure

1. Incubation bottles

Before use, clean all bottles with a detergent, rinse them thoroughly, and then rinse them with "No-Chromix" or chromic acid solution. Pour the acid from bottle to bottle, stopper, and swirl. Rinse thoroughly first with tap water and then triple rinse with distilled water and let drain dry. Drain the bottles well. (**CAUTION:** "No Chromix" and chromic acid are both very corrosive. Extreme care should be taken to avoid contact with skin or clothes). Dirty BOD bottles will cause errors in the test. Thoroughly rinsing with distilled water is especially important; otherwise the acid left in the bottles will lower the pH and kill the bacteria.

2. Sample preparation

a. pH

Neutralize samples that have a high or low pH to pH 6.0 to 8.0 with 1N H_2SO_4 or 1N NaOH solutions (Reagents 1. and 2.).

b. Seeding the sample

It is necessary to have present a population of microorganisms capable of oxidizing the biodegradeable organic matter in the sample. In some samples, including chlorinated domestic wastewaters, untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values, the bacteria were killed or never present. For this reason, bacteria is added to each sample by the analyst. This process is referred to as seeding a sample. Add 4 mL of seed solution (Reagent 11.) to each individual BOD bottle.

c. Dilutions

Dilution of the samples is necessary to match the available dissolved oxygen with the oxygen demand of the sample. Several dilutions of every sample are required to insure this match-up. Dilutions that result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after 5 day incubation produce the most reliable results.

Make several dilutions of each prepared sample to obtain DO uptake in the range mentioned above. Experience with particular samples (samples from known clients) will eventually permit use of a smaller number of dilutions, however, do not use less than three dilutions per sample. A client dilution list is located near the DO meter for reference. In the

absence of prior knowledge, use the following guidelines for dilutions: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

Prepare dilutions directly into individual BOD bottles. Pipet the required volume of sample into the BOD bottle, add 4 mL seed solution (Reagent 11.), and fill the rest of the bottle with dilution water, allowing no air bubbles. Stopper the bottle making sure not to trap any air.

If inhibition of nitrification is desired (to obtain carbonaceous result only) add 4 mL of the inhibitor seed solution (Reagent 12.) directly to the BOD bottle instead of the normal seed solution.

In addition to regular samples prepare two blank BOD bottles by filling them with dilution water only. Also prepare two seed control bottles by adding 25 mL seed solution directly to the bottles and filling with dilution water. These will serve as a correction factor for seed DO uptake.

III. Analysis Procedure

A. Theory

The 5-day BOD method analysis consists of filling an airtight bottle to overflowing with sample and incubating it at the specified temperature for five days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Alternative seeding, dilution, and incubation conditions can be chosen to mimic receiving-water conditions, thereby providing an estimate of the environmental effects of wastewaters and effluents.

B. Method

1. Azide modification (Winkler method)

This method is used to determine dissolved oxygen in the BOD bottles and the dilution water (by titration). Set up two bottles (blank dilution water) to perform the Winkler test-one to determine the initial DO and the second, after incubation, to determine the final DO.

To 300 mL dilution water in the BOD bottle, add 2.0 mL manganese sulfate solution (Reagent 8.), followed by 2.0 mL alkaline-iodide-azide reagent (Reagent 9.). Put the stopper in, excluding air bubbles, and invert several times to mix the solution. Allow precipitate to settle to the lower third of the bottle, unstopper it and add 2.0 mL conc. sulfuric acid. Restopper the bottle and invert several times until all of the precipitate dissapears. pale yellow to amber color indicates there is oxygen present in the sample.

Pour the contents of the BOD bottle into a 500 mL Erlenmeyer flask. Titrate with PAO titrant (Reagent 10.) to a pale yellow color and add several drops of starch indicator solution. Continue the titration to the first disappearance of blue color. For titration of a 300 mL sample, 1.0mL of .0375N PAO equals 1.0 mg/L dissolved oxygen.

Calibrate the meter to read the same as the DO measured by the Winkler method before reading the initial DO values of the samples, standards and blanks. Perform the Winkler test on each new batch of dilution water. If a new container of dilution water is prepared in the middle of a run, perform the Winkler test on a 300 mL aliquot and record the result. Do not reset the DO meter at this time, instead continue the run with the initial calibration.

When taking the final DO readings, perform the Winkler test on one of the dilution water blanks (which has been incubated) and reset the DO meter to the value obtained. Read the second blank and the rest of the samples after meter has been reset.

2. Determination of initial DO

After calibrating the DO meter, initial DO can be measured for each BOD bottle. If the sample contains materials that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If rapid initial DO uptake is insignificant, the time period between preparing dilution and measuring initial DO is not critical.

3. Incubation

Incubate all BOD bottles containing desired dilutions, seed controls, dilution water blanks, and standards, at 20 degrees Celsius (plus or minus one degree) in the dark. It is important that the bottles be airtight; this is accomplished by a water seal. Add water around the flared mouth of the bottle and put a Dixie cup over it to prevent evaporation during incubation.

4. Determination of final DO

At the end of the 5 day incubation period and after recalibrating the DO meter with the incubated dilution water (mentioned in the Winkler section above), determine DO in sample dilutions, blanks, and standards.

IV. Quality Assurance/Quality Control

Quality control procedures described by the EPA in VOL. 49, No. 209 of the Federal Register have been implemented by EMS to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. In addition to this, internal QAQC is routinely performed on all types of sample matrices. This QAQC includes analytical blanks and standards, matrix spikes, and matrix spike duplicates.

QAQC samples are done per BOD run as follows:

<u>Dilution Water Blanks</u> - 2 for each batch of samples

<u>Seed Control Samples</u> - 2 for each batch of samples

<u>ICV01</u> - one per week: 10, 15, 20(2x), mLs into BOD bottle (EPA)

<u>CCV01</u> - six per run: dilutions of glucose-glutamic acid standard
high std- (Reagent 4.) 3, 6, and 9 mLs into BOD bottles
low std- (Reagent 5.) 25, 50, and 100 mLs into BOD bottles
Be sure to seed all prepared standards.

<u>NOTE</u>: The CCV dilution that best represents results having a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after 5 day incubation is accepted as the CCV for that run.

<u>DUP01</u> - one per every ten samples: replicability <= 20%

The relative % difference (%RPD) is calculated between the sample and the sample duplicate. The formula is:

$$\%RPD = \frac{|D1-D2|}{D1+D2} \times 100$$

D1-sample value D2-sample duplicate value

All BOD data generated is reviewed by the group leader section leader for completeness and accuracy before the samples are reported. The reviewer is responsible for making sure that all relevant information has been recorded correctly and that all QAQC has been completed. No one can review their own data. Each run sheet is initialled and dated by the reviewer.

V. <u>Calculations</u>

The seed material added directly to sample or to seed control bottles has a BOD value. This value must be taken into account when calculating the BOD of the samples, blanks, and standards. The following equation is used when samples are seeded:

$$BOD\ mg/L = \frac{(DOi-DOf) - (Bi-Bf)\ f}{P}$$

where:

DOi = initial DO,
DOf = final DO,
Bi = DO of seed control before incubation,
Bf = DO of seed control after incubation, and
f = ratio of seed in diluted sample to seed in seed control = (% seed in diluted sample)/(% seed in seed control). Equal to 4ml/25ml in this method.

Report results as CBOD if nitrification is inhibited.

VI. Interferences/Troubleshooting

VII. Safety Precautions

When working in the laboratory, wear protective equipment including safety glasses, lab coat, and gloves. There are several extremely hazardous reagents involved in the test. Sulfuric acid used to clean the bottles, to neutralize basic samples, and in the Winkler DO procedure can cause serious burns to the skin. The alkaline-azide reagent is also very corrosive. Care should be taken to avoid contact with any reagent.

VIII. Cleanup and Disposal

After the BOD test has been completed, samples can be diposed of down the drain. Flush with copius amounts of cold water. BOD bottles should be cleaned with "No chromix" and rinsed with tap water and DI water. Replace all lids on reagent bottles and make sure area is cleaned up.

IX. References

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 405.1.

Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989, Method 5210.

The Biochemical Oxygen Demand Test Laboratory Manual, EMS Laboratories, Inc. (Reid, Quebe, Allison, Wilcox & Associates), 1982.

EMS Test Codes: G301.1 Revision Date_____
Method Quote:

DO NOT DUPLICATE

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CHEMICAL OXYGEN DEMAND

Referenced Procedures - (USEPA Method 410.4)

BY _____ DATE_____

I. Introduction

Although BOD is a measure of the quantity of oxygen utilized by suitable aquatic microorganisms in water, the test is rather time-consuming and cumbersome to perform. Chemical oxygen demand, COD, is a much more easily determined parameter. The COD test is a measurement of the amount of organic matter present in water that is subject to oxidation by dichromate ion in 50% sulfuric acid. The COD of water may differ appreciably from the BOD. The presence of poorly biodegradable compounds in water will result in a COD higher than the BOD. The easier and faster COD test is often substituted for the BOD test, although there is not always a definite correlation between them.

A. Test - G301.1
B. Method Detection Limit - 10mg/L
C. Containers - 1L Plastic cube containers
D. Preservative - Cool, 4 degrees Celsius, H_2SO_4 to pH<2
E. Regulatory Holding Time - 28 days
F. Recommended Holding Time - 7 days

II. Extraction Procedures

A. Theory

During the digestion process, each dichromate molecule and organic molecule react in which the dichromate loses three oxygen atoms. The oxygen lost reacts with hydrogen or carbon to form water or carbon dioxide. Since it is impossible to measure this increase when a large amount of water is present, the color change occurring with the dichromate is measured.

The chromium (Cr) atoms in the dichromate have a valence of 6+ and an orange color in solution. When the dichromate gives up the three oxygen atoms during the digestion process, each chromium gains three electrons which changes its valence from 6+ to 3+. At this time the color of the solution changes from orange to blue-green.

The final amount of Cr(III) produced in the reaction is determined by the amount of blue-green color that is present. This amount is determined spectrophotometrically by measuring the absorbance at 600 nanometers and comparing it to a set of standards appropriate for each scale. The more oxidizable material in each sample, the more blue-green color will be present. For the low scale (0-200ppm)

the absorbance is read at 440 nanometers with the blank being the 200ppm standard and the HIGH being the zero standard. At this wavelength, the "disappearance of the blue-green color" is being measured.

B. APPARATUS
1. Hach COD Reactor, 150 Degrees Celsius
2. Hach COD Digestion Vials
3. Sequoia Turner (Model 690) Spectrophotometer
4. Oxford Pipet, 1-5ml (0.1 increments)
5. Repipet II, 0-5ml (0.05 increments)

C. REAGENTS
1. Catalyst Solution: 4.09kg bottle of concentrated sulfuric acid with 22 grams of silver sulfate added.
2. Digestion Solutions:
   a. High: Add 10.2g potassium dichromate ($K_2Cr_2O_7$), 167ml conc sulfuric acid, and 33.3g of mercuric sulfate to 500ml of distilled water and let cool. Dilute to one liter.
   b. Low: Same as above with the exception of using 2.04g of potassium dichromate.
3. Potassium Hydrogen Phthalate (KHP): Dissolve 850mg KHP (dried at 105 degrees Celsius for one hour and desiccated) into 800ml of distilled water. Dilute to one liter (1000ppm).
4. Dilution of stock KHP (1000ppm) to make standard working solutions for each the high and low scale.
5. 1 + 1 H_2SO_4 COD vial wash solution.

D. Procedure
1. Mix 30ml of digestion solution with 70ml of catalyst solution in a 500ml Erlenmeyer flask. Swirl the mixture carefully, holding the flask away from the face (caution: exothermic reaction). Allow solution to cool. Pour the solution into the Repipet II and allow the precipitate to settle.
2. Preheat COD reactor to 150 degrees Celsius.
3. Hold the digestion vial at a 45 degree angle and add 5ml of the digestion/catalyst solution to the vial from the Repipet.
4. Homogenize the sample.
5. Using the Oxford Pipet, pipet 2.5ml of the sample to the vial containing the digestion/catalyst solution. Cap the vial immediately.
6. Invert the vial 10 times. **Caution:** the vial will become very hot during mixing. Do not mix the vial near face.
7. Place vial into preheated COD reactor. Heat vial for 2 hours at 150 degrees Celsius. Remove and cool to room temperature.

III. COD Analysis

A. The Sequoia Turner Spec21 is turned on and allowed to warm up. The high scale is set at 600nm and the low scale at 440nm.
B. At 600nm (high scale), the blank is the reference zero while the 1000ppm standard is the extreme high end of the scale. (eg; zero has the least blue-green color-1000ppm standard has the most).
C. At 440nm (low scale), the 200ppm standard is the reference zero while the blank is the high end of the scale.
D. A linear plot is established for either scale using the prepared standards (absorbance vs. concentration).
E. Samples are read and compared to the linear plot and a COD result is determined.
F. Dilution may be necessary if the sample is higher than the 1000ppm standard.

IV. Quality Control

A. BLA01 - one per run
B. PER01 - one per run, recovery must be
C. DUP01 - one per run, RPD must be less than
D. SPI01 - one per run, recovery must be

V. Calculation

$$\text{COD as } mgO_2/L = \frac{mgO_2 \text{ in final volume} \times 1000}{\text{ml sample}}$$

VI. Interferences/Troubleshooting

High levels of chloride will cause a positive interference. The addition of mercuric sulfate in the digestion solution will complex the chloride (also bromide and iodide). Nitrate will also cause a positive interference. The addition of 10mg sulfamic acid to 1.1mg O_2/mg NO_2^- will eliminate this interference. Other interferences include ferrous iron, sulfide, manganous manganese, etc.

Straight chained aliphatic compounds cause a negative interference because the dichromate is not a powerful enough oxidant to oxidize them. Silver sulfate is added as a catalyst so oxidation will be complete.

VII. SAFETY

A. Place reactor into a hood to minimize hazard in case of vial breakage.
B. When mixing the digestion/catalyst solution in the vial, hold the vial away from the face. A great deal of heat is generated which can crack the vial.

APPENDIX I

SITE HEALTH AND SAFETY PLAN

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I.1.0 GENERAL

The RI/FS investigation program to be implemented to satisfy the requirement as presented in the SOW will involve drilling and sampling within the limits of the Four County Landfill Site (Site). During these operations, personnel may come in contact with sediments, groundwater and surface water which potentially contain hazardous materials. To ensure that any direct contact with potentially contaminated material by Site personnel is minimized, a Site-specific Health and Safety Plan (HSP) has been developed, as presented herein. This HSP has been developed to ensure the following:

i) that Site personnel are not adversely exposed to the compounds of concern;

ii) that public welfare or the environment are not adversely impacted by off-Site migration of contaminated materials due to work activities at the Site; and

iii) compliance with applicable governmental and non-governmental (American Conference of Governmental Industrial Hygienist) regulations and guidelines. In particular, the amended rules of the Occupational Safety and Health Act for Subpart H of Part 1910 (Title 29 Code of Federal Regulations (CFR) Part 1910.120) will be implemented for all Site work.

For the purpose of this HSP, all sampling and investigative activities carried out on Site involving contact with potentially contaminated materials will be considered contaminated operations requiring personal protective equipment (PPE). Similar activities occurring off Site are considered non-contaminated operations requiring a modified level of PPE from that for on-Site work. A detailed description of the PPE required is presented in Section I.8.0.

All sampling and investigative operations at the Site will be conducted in accordance with the provisions of the HSP. Cost and/or

scheduling considerations will not be considered as justification for modifying this plan.

I.2.0 SITE CHARACTERIZATION AND HAZARD ANALYSIS

The Site was used as a sanitary landfill from 1972 to 1977, where unlined waste deposits were covered with backfill. From 1978 to 1984 the Site accepted "separate area waste" including paint sludge, municipal wastewater treatment sludge, asbestos and liquids which were deposited in unlined cells. From 1980 to 1989 the Site accepted RCRA hazardous wastes which were deposited in synthetically-lined disposal cells (A, B and C). Based on various historical investigations, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOC) and inorganic compounds have been detected in the sampled media that is associated with the Site.

Potential hazards associated with activities to be conducted at the Site include:

i) drilling operations;

ii) material and equipment handling injuries;

iii) contact with contaminated sediments, water and leachate; and

iv) chemical inhalation.

Risks associated with these activities will be minimized by implementing engineering controls and the proper use of personal protective equipment (PPE). Table I.1 summarizes potential hazards associated with the Site.

TABLE I.1

SITE HAZARD ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Site Activities	*Hazards*	*Prevention*
Groundwater Sampling	Chemical hazards due to inhalation and dermal contact	Proper use of PPE
	Exposure to temperature extremes	Monitor for heat or cold stress
	Physical hazards including steep grades and unstable surfaces	Use "buddy system" during Site activities
Well Abandonment	Chemical hazards due to inhalation and dermal contact	Proper use of PPE
	Working around drilling equipment	Maintain a safe distance from drill rig when it is in use
	Exposure to temperature extremes	Monitor for heat or cold stress
	Sharp objects	Wear cut resistant work gloves
	Slip, trip, fall	Clear walkways and work area of obstructions
	High noise levels	Use hearing protection
	Physical hazards including steep grades and unstable surfaces	Use "buddy system" during Site activities

TABLE I.1

SITE HAZARD ANALYSIS
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Site Activities	*Hazards*	*Prevention*
Sediment and Surface Water Sampling	Chemical hazards due to inhalation and dermal contact	Proper use of PPE
	Exposure to temperature extremes	Monitor for heat or cold stress
	Physical hazards including steep grades and unstable surfaces	Use "buddy system" during Site activities
Site Maintenance Activities	Chemical hazards due to inhalation and dermal contact	Proper use of PPE
	Exposure to temperature extremes	Monitor for heat or cold stress
	Physical hazards including steep grades and unstable surfaces	Use "buddy system" during Site activities

I.3.0 BASIS

The Occupational Safety and Health Administration (OSHA) Standards and Regulations contained in Title 29, CFR, Parts 1910 and 1926 (29 CFR 1910 and 1926) including the amended sections in 29 CFR 1910.120 and current Threshold Limit Values (TLVs) as provided by the American Conference of Governmental Industrial Hygienists (ACGIH) provide the basis for this Health and Safety Plan. Some of the specifications within this section are in addition to OSHA regulations and reflect the positions of the USEPA, the National Institute for Occupational Safety and Health (NIOSH) and the United States Coast Guard (USCG) regarding procedures required to ensure safe operations at potential hazardous waste sites.

The safety and health of the public and on-Site personnel and the protection of the environment will take precedence over cost and schedule considerations for all project work. The Site maintenance contractor will designate an on-Site individual as Site Health and Safety Officer (HSO) to implement the HSP during Site maintenance activities. CRA will designate an HSO to implement the HSP during field sampling activities. The HSOs will be responsible for decisions regarding when work will be stopped or started for health or safety considerations.

I.4.0 RESPONSIBILITIES AND ADMINISTRATION

The HSO will supervise the implementation of the Health and Safety Plan and will be responsible for all decisions regarding operations and work stoppages due to health and safety considerations.

The responsibilities of the HSO are as follows:

i) be responsible for implementation of the HSP at the initiation of Site work;

ii) conduct the initial briefing sessions for all on-Site personnel with regard to the HSP and other safety requirements to be observed during field sampling, including:

   a) potential hazards,
   b) personal hygiene principles,
   c) personal protective equipment,
   d) respiratory protection equipment usage, and
   e) emergency procedures dealing with fire and medical situations;

iii) review and modify the HSP as more information becomes available concerning the hazardous materials involved, and review all monitoring reports;

iv) supervision and enforcement of safety equipment usage;

v) supervision and inspection of equipment cleaning;

vi) personnel training in safety equipment usage and emergency procedures;

vii) monitoring of the health and safety program under direction of an industrial hygienist;

viii) suspend work activity if unsafe working conditions develop;

ix) inform workers of the nature of chemical exposure risk as required by the "Right-to-Know" Law;

x) recommend medical examination when worker appears to require it;

xi) coordination of emergency procedures; and

xii) assure that safety equipment is provided, maintained and accessible to Site personnel.

I.5.0 MEDICAL SURVEILLANCE

In accordance with requirements detailed in 29 CFR 1910.120 and 29 CFR 1910.134, all Site personnel who will come in contact with potentially contaminated materials will have received, within one year prior to starting field activities, medical surveillance by a licensed physician or physician's group.

Medical records for all on-Site sampling personnel will be maintained by their respective employers. The medical records will detail the tests that were taken and will include a copy of the consulting physician's statement regarding the tests and the employee's suitability for work.

The medical records will be available to the employee or his designated representative upon written request, as outlined in 29 CFR 1910.120, Section (f).

Each employer will ensure that its personnel involved in on-Site work will have all necessary medical examinations prior to commencing work which requires respiratory protection or exposure to hazardous materials. Personnel not obtaining medical certification will not perform work within contaminated areas.

Interim medical surveillance will be completed if an individual exhibits poor health or high stress responses due to on-Site activity or if an accidental exposure to elevated concentrations of contaminants occurs.

I.6.0 TRAINING

CRA will require that all personnel actively engaged in RI/FS and/or Site O&M activities, prior to entering the Site, complete training sessions in accordance with 29 CFR 1910.120. This training shall consist of a minimum of 40 hours of instruction off Site and three days of actual field inspection under direct supervision. Each employer will maintain documentation stating that its on-Site personnel have complied with this regulation.

Prior to commencing Site activities, a Site-specific initiation session will be conducted. This session will be used to instruct the on-Site personnel as to what the potential Site hazards are. Topics covered will include:

i) Site-specific health and safety hazards;
ii) level of PPE required;
iii) safe use of equipment;
iv) decontamination procedures; and
v) emergency response procedures.

All personnel who attend this session will sign a Training Acknowledgment Form, an example of which is presented as Attachment I.

I.7.0 WORK AREAS

The HSO will delineate work areas in the field and will limit equipment, operations and personnel in each of the areas as defined below:

i) Exclusion Zone - This zone will include the area within the immediate vicinity of active sampling locations and the landfill. The Exclusion Zone will be delineated in the field at active sampling locations prior to commencing work at each sampling location.

Access to the Exclusion Zone will be restricted to personnel who are wearing the proper PPE, have received the required medical examination, and have undergone the required training. Eating, drinking, or smoking is prohibited in this area.

ii) Contamination Reduction Zone - this will be established adjacent to the exclusion zone. Procedures will be implemented to prevent active or passive contamination from the exclusion zone.

iii) Support Zone - This is the area in the vicinity of the Site maintenance building.

I.8.0 PERSONAL PROTECTIVE EQUIPMENT

All on-Site personnel are required to be equipped with PPE appropriate for the nature of work being completed. All safety equipment and protective clothing will be kept clean and well-maintained.

Safety equipment and apparel as required on Site will be Level D or Level C protective equipment within the Exclusion Zone.

The Level D protective equipment consists of the following:

i) work boots with steel toe and shank;
ii) hard hat;
iii) latex and/or cotton gloves; and
iv) safety glasses and/or goggles.

Level C protective equipment may be used on Site if the action levels in Section I.9.0 are exceeded, Level C CPPE consists of the following:

i) individually assigned full-facepiece air-purifying respirators (NIOSH approved), with appropriate cartridges for organic vapors and particulates. Respirators should be available at all times and donned when required as indicated by air monitoring;

ii) chemical-resistant disposable coveralls;

iii) latex and/or cotton inner gloves;

iv) nitrile outer gloves;

v) work boots with steel toe and shank;

vi) chemical-resistant overboots or booties;

vii) hard hat; and

viii) safety glasses and/or chemical-resistant goggles.

If work is conducted beyond the Site boundary, it is anticipated that Level D PPE will be required.

Additional protective equipment usage guidelines to be implemented include:

i) prescription eyeglasses in use on the Site will be safety glasses;

ii) contact lenses will not be permitted;

iii) all disposable or reusable nitrile, latex and/or cotton gloves worn on the Site will be changed, decontaminated or discarded at the end of each day;

iv) during periods of respirator usage, respirator cartridges and filters will be changed daily, or upon breakthrough, whichever occurs first;

v) on-Site personnel who have not passed a respirator fit test will not be permitted to enter or work in the Exclusion Zone. Personnel will not be permitted to have beards, or long sideburns or mustaches as these interfere with a proper fit of the respirator;

vi) all PPE worn on Site will be decontaminated or discarded at the end of each work day;

vii) duct tape will be used to ensure that disposable coveralls and gloves are tightly secured when personnel are working within the Exclusion Zone; and

vii) no watches, rings or other accessories will be permitted during drilling and sampling activities.

I.9.0 RESPIRATOR PROGRAM

Prior to arriving at the Site, all on-Site personnel will have received training in the use of, and have been fit tested for a full-facepiece respirator.

A photoionization detector will be used to determine if organic vapors and some inorganic gases are present. A background reading will be established prior to commencing work activities at each monitoring well or sampling location.

Action levels to determine the level of respiratory protection necessary during field activities will be:

Sustained Photoionization Organic Vapor Reading Above Background	*Protection Level*
1 - 25 ppm	full-facepiece air purifying respirator (Level C)
>25 ppm	shut down activities

A combustible gas indicator will be used to monitor for oxygen/combustible gases/carbon monoxide/hydrogen sulfide and a monotox unit will be used to monitor for hydrogen cyanide.

Work will be stopped and the work area will be allowed to vent if monitoring indicates that any of the following conditions exist:

i) toxic gases are present at concentrations which present Immediate Danger to Life and Health (IDLH) conditions, or in excess of the protection factor afforded by the air purifying respirator (whichever is lower); or

ii) the oxygen content of the air is less than 19.5 percent;

iii) hydrogen sulfide levels exceed 2 ppm;

iv) carbon monoxide levels exceed 20 ppm;

v) hydrogen cyanide levels exceed 2 ppm; or

vi) organic vapor concentrations in the breathing zone exceeds 25 ppm.

Air monitoring should continue, at a safe distance, if operations are stopped due to action level exceedences, to determine if a threat to the surrounding community exists.

I.10.0 JUSTIFICATION

These action levels assume that all NIOSH criteria for using an air purifying respirator (APR) have been met. An APR can typically be worn in concentrations of up to 50 times the TLV for a given contaminant. Most of the contaminants at the Site have TLVs or PELs higher than 1 ppm. Because of differences in sensitivities with direct reading instruments, a 50 percent safety factor is included when determining action levels. Therefore, the calculation would be:

1 ppm (TLV) x 50 (protection factor) x 0.5 (50% safety factor) = 25 ppm

A non-specific total gas and vapor analyzer such as a photoionization detector, will be used to provide a relative index for cumulative effects of multiple similar compounds.

The primary routes for exposure to contaminants for individuals performing RI/FS investigative tasks include direct contact, ingestion and inhalation. The risk of exposure due to direct contact and ingestion will be minimized through the proper use of PPE as described in Section I.8.0 and by exercising ordinary care during sampling activities. In order to minimize exposure by the inhalation pathway, the respirator and air monitoring programs discussed in Sections I.9.0 and I.12.0 will be undertaken.

Table I.2 presents a summary of the contaminants of concern for the inhalation pathway and the associated TLVs and PELs for these compounds. The contaminants of concern list was developed using a worst-case scenario on the basis of data developed during previous sampling rounds at the Site. Concentrations of VOCs were compared against the TLVs and PELs. It was assumed that the entire concentration of VOCs would volatilize into the air and would be present at their maximum concentration (in parts per million) observed in groundwater, within the breathing zone of the work area. VOCs with concentrations in groundwater exceeding the TLVs or PELs were therefore, selected as contaminants of concern. Also selected as contaminants of concern were common landfill gases such as hydrogen sulfide, carbon monoxide, carbon dioxide, methane and hydrogen cyanide.

TABLE I.2

CONTAMINANTS OF CONCERN
FOUR COUNTY LANDFILL SITE
FULTON COUNTY, INDIANA

Compound	*ACGIH TLV (ppm)*	*OSHA PEL (ppm)*
Acetone	750	750
Benzene	1	1
Carbon dioxide	5,000	10,000
Carbon monoxide	25	35
Carbon tetrachloride	5	2
Chlorobenzene	10	75
Chloroform	10	2
1,1,2,2 Tetrachloroethene	1	1
Hydrogen cyanide	10	4.7
Hydrogen sulfide	10	10
Methane	--	--
Methyl isobutyl ketone	50	50
Methylene chloride	50	500
Tetrachlorethene	25	25
1,2-Dichloroethane	10	1
Tetrahydrofuran	200	200
Toluene	50	100

Chemical specific information is presented as Attachment II of this HSP.

I.11.0 PERSONAL HYGIENE

All personnel performing or supervising work within the Exclusion Zone are required to observe and adhere to the personal hygiene-related provisions of this section.

On-Site personnel found to be disregarding the personal hygiene-related provisions of this HSP will, at the discretion of the HSO, be barred from the Site.

The following equipment/facilities will be made available for the personal hygiene of all on-Site personnel:

i) suitable disposable outerwear, gloves, respiratory protection and footwear on a daily basis for the use of on-Site personnel;

ii) disposal containers for used disposable outerwear; and

iii) potable water and a suitable sanitation facility.

The HSO will enforce the following regulations for personnel actively participating in the field sampling program and Site maintenance activities:

i) on-Site personnel will wear appropriate PPE when in the Exclusion Zone;

ii) used disposable outerwear will not be reused if deemed to be unsuitable to provide the necessary protection, and when removed, will be placed inside disposal containers provided for that purpose;

iii) smoking, eating and drinking will be prohibited within the Exclusion Zone. These activities will be permitted only within the area of the Support Zone; and

iv) on-Site personnel will thoroughly cleanse their hands, face, neck area and other exposed areas before smoking, eating or drinking and before leaving the Site.

I.12.0 AIR MONITORING

During the progress of active work, air quality on Site will be monitored. Monitoring will be conducted on a daily basis and additionally as required by special or work-related conditions. Air monitoring will be completed within the breathing zone at each active work site.

The daily monitoring program will consist of monitoring with a photoionization device for organic vapors; combustible gas indicator hydrogen sulfide, and carbon monoxide indicator; and hydrogen cyanide using a monotox unit.

Identification of volatile organic vapor levels in excess of the action levels cited in Section I.9.0 shall be reported to the HSO, who will determine when PPE should be upgraded and operations be shut down and restarted.

If work is stopped because action levels have been exceeded, air monitoring will continue from a safe distance to determine if there is a threat to the surrounding community.

I.13.0 COMMUNICATIONS

Emergency numbers including police, fire, ambulance, hospital and appropriate Regulatory agencies (Table I.3) will be prominently posted near the Site telephone(s).

A route map to the nearest emergency medical facility (Attachment III) will be posted in each vehicle. Prior to initiating Site activities, the emergency medical facility will be notified of Site activities to ensure preparedness to respond to any Site-related injuries.

TABLE I.3

EMERGENCY CONTACTS
FOUR COUNTY LANDFILL

JNTY, INDIANA

Agency/Firm	*Emergency Telephone Number*	*Business Telephone Number*
Leiters Ford Fire Department	(219) 542-4491	--
Fulton County Sheriff	(219) 223-2819	--
Ambulance	(219) 223-4911	--
Woodlawn Hospital	(219) 223-4911	(219) 223-3141
Poison Control Center	(800) 942-5969	--
National Response Center	(800) 424-8802	--
CRA Industrial Hygiene		
-Chicago (Matt Lazaric)	--	(708) 299-9933
-Corporate (Mitch Bergner)	--	(612) 639-0913
CRA Project Manager (Bruce Clegg)	--	(708) 299-9933

I.14.0 EMERGENCY AND FIRST AID EQUIPMENT

Safety equipment will be available for use by Site personnel and will be located and maintained on Site. The safety equipment will include, but is not limited to, the following:

i) portable emergency eye wash;

ii) two ABC type dry chemical fire extinguishers; and

iii) approved first-aid kit for a minimum of ten personnel.

I.15.0 EMERGENCY RESPONSE PLAN

Prior to commencing work involving intrusive activities, CRA will coordinate development of an off-Site emergency contingency plan. This plan is intended to provide immediate response to a serious Site occurrence such as explosion, fire or migration of significant quantities of toxic or hazardous materials from the Site to adjacent areas.

CRA will designate an individual as the Safety Supervisor (SS), who will be responsible for implementing this plan. The SS will be thoroughly familiar with all aspects of the Site including facility layout, all operations and activities on Site, and the location and characteristics of waste handled.

Prior to commencing Site activities the SS will discuss Site activities with the appropriate authorities including the State, Fire and Hospital. These meetings will serve to identify the SS through whom all information and coordination will occur in the event of a serious incident.

Prior to commencing work, the HSO will inform local emergency response personnel of the activities at the Site. This is intended to provide immediate response to a serious Site occurrence such as injury, explosion or fire.

In the event of injury to on-Site personnel, the following protocol will be followed:

i) notify the Health and Safety Officer;

ii) contact the designated hospital;

iii) decontaminate personnel if possible, and administer appropriate first aid. If personnel cannot be decontaminated, alert hospital to possible problems of contamination; and

iv) transport personnel to the medical facility along a predefined route.

In the event of an emergency on Site, the following protocol will be followed:

i) notify the Health and Safety Officer;

ii) evacuate the work area;

iii) the HSO will perform a head-count to ensure that all personnel have exited the area;

iv) contact the safety supervisor; and

v) the safety supervisor will notify the appropriate emergency response personnel;

vi) provide the safety supervisor and emergency response personnel with useful information;

It will be the responsibility of the safety supervisor and emergency response personnel to determine whether or not there is any danger to the surrounding community. If there is any danger to the surrounding community it is the responsibility of the safety supervisor, emergency response personnel and local authorities to evacuate the affected areas as quickly and safely as possible.

I.16.0 EQUIPMENT AND PERSONNEL DECONTAMINATION

During the initiation of the field investigative program, procedures will be implemented to reduce the amount of contact of both personnel and equipment with the waste constituents. These procedures include the following:

i) proper work practices that would lead to minimal direct contact with potentially contaminated material; and

ii) use of disposable equipment and clothing as much as practicable.

All equipment leaving the Exclusion Zone which came in contact with potentially contaminated material will be decontaminated.

Personnel decontamination, if required, will take place at the exit from the Exclusion Zone and will, as a minimum, consist of a glove wash with detergent and removal of gloves, disposable suit, and hard hat.

All personnel will remove their protective clothing and wash their hands, face, neck area and other exposed areas before entering the lunch and break areas to eat, drink or smoke.

Used PPE will be placed in plastic bags and then stored in 55-gallon drums. PPE will be segregated from general refuse and disposed of in accordance with federal, state and local requirements.

I.17.0 CONTAMINATION MIGRATION CONTROL

All vehicles and equipment used within the Exclusion Zone will be decontaminated on Site as determined necessary by the HSO prior to leaving the Site. Decontamination, when required, will consist of the thorough cleaning of those parts of the equipment which come in contact with potentially contaminated material. The HSO will certify that each piece of equipment is clean or has been decontaminated prior to removal from the Site.

Personnel engaged in vehicle decontamination will wear protective equipment including suitable disposable clothing, respiratory protection and face shields.

ATTACHMENT I

TRAINING ACKNOWLEDGMENT FORM

TRAINING ACKNOWLEDGEMENT FORM

Please Print:

NAME: _____

ADDRESS: _____

SOCIAL SECURITY NUMBER: _____

EMPLOYER: _____

JOB SITE: _____

I have attended and understood the mandatory Site-specific initiation session for the above-referenced job site. This program referenced the following topics:

i) known potential hazards on Site;

ii) level of personal protection equipment required;

iii) emergency procedures for the Site; and

iv) have received explanation of the basics of the Health and Safety Plan.

I further confirm that I have the required 40 hours of training to comply with 29 CFR 1910.120 and have a respirator for which I have been fit tested.

_____
Signature

ATTACHMENT II

MATERIAL SAFETY DATA SHEETS

ORDER NO: 210745254
PROD NO: 04006155

VAN WATERS & ROGERS INC. 1600 NORTON BLDG. SEATTLE, WA 98104-1564

EMERGENCY ASSISTANCE

FOR EMERGENCY ASSISTANCE INVOLVING CHEMICALS CALL CHEMTREC (800) 424-9300.

FOR PRODUCT AND SALES INFORMATION

CONTACT YOUR LOCAL VAN WATERS & ROGERS BRANCH OFFICE

PRODUCT IDENTIFICATION

PRODUCT NAME: ACETONE
COMMON NAMES/SYNONYMS: ACETONE; 2-PROPANONE
FORMULA: C3 H6 O
HAZARD RATING (NFPA 704)
HEALTH: 1
FIRE: 3
REACTIVITY: 0
SPECIAL: NONE

CAS NO.: 67-64-1
VW&R CODE: T1018

DATE ISSUED: 12/88
SUPERCEDES: 08/87
HAZARD RATING SCALE:
0=MINIMAL 3=SERIOUS
1=SLIGHT 4=SEVERE
2=MODERATE

HAZARDOUS INGREDIENTS

COMPONENT	%	EXPOSURE LIMITS, PPM OSHA PEL	ACGIH TLV	OTHER LIMIT	HAZARD
ACETONE	>99	1000	750	1000 (ACGIH STEL)	FLAMMABLE; IRRITANT

PHYSICAL/CHEMICAL CHARACTERISTICS

BOILING POINT, DEG F: 133
MELTING POINT, DEG F: -142
SPECIFIC GRAVITY (WATER=1): 0.79
APPEARANCE AND ODOR: CLEAR, COLORLESS LIQUID; SWEET ODOR

VAPOR PRESSURE, MM HG/20 DEG C: 184
VAPOR DENSITY (AIR=1): 2.0
WATER SOLUBILITY, %: 100
EVAPORATION RATE (BUTYL ACETATE=1): 14

FIRST AID MEASURES

IF INHALED: REMOVE TO FRESH AIR. GIVE ARTIFICIAL RESPIRATION IF NOT BREATHING. GET IMMEDIATE MEDICAL ATTENTION.

IN CASE OF EYE CONTACT: IMMEDIATELY FLUSH EYES WITH LOTS OF RUNNING WATER FOR 15 MINUTES, LIFTING THE UPPER AND LOWER EYELIDS OCCASIONALLY. GET IMMEDIATE MEDICAL ATTENTION.

IN CASE OF SKIN CONTACT: IMMEDIATELY WASH SKIN WITH LOTS OF SOAP AND WATER. REMOVE CONTAMINATED CLOTHING AND SHOES; WASH BEFORE REUSE. GET MEDICAL ATTENTION IF IRRITATION PERSISTS AFTER WASHING.

SWALLOWED: IF CONSCIOUS, IMMEDIATELY INDUCE VOMITING BY GIVING 2

GLASSES OF WATER AND STICKING A FINGER DOWN THE THROAT. GET IMMEDIATE MEDICAL ATTENTION. DO NOT GIVE ANYTHING TO AN UNCONSCIOUS OR CONVULSING PERSON.

HEALTH HAZARD INFORMATION

PRIMARY ROUTES OF EXPOSURE: INHALATION, SKIN OR EYE CONTACT.

SIGNS AND SYMPTOMS OF EXPOSURE

INHALATION: PROLONGED OR REPEATED EXPOSURE OR BREATHING VERY HIGH CONCENTRATIONS MAY CAUSE HEADACHES, NAUSEA, VOMITING, DIZZINESS, OTHER CENTRAL NERVOUS SYSTEM EFFECTS, CONVULSIONS, AND IN EXTREME CASES, UNCONSCIOUSNESS AND DEATH.

EYE CONTACT: VAPORS WILL IRRITATE THE EYES. LIQUID AND MISTS WILL IRRITATE AND MAY BURN THE EYES.

SKIN CONTACT: BRIEF CONTACT MAY DRY THE SKIN. PROLONGED OR REPEATED CONTACT MAY IRRITATE THE SKIN, CAUSING DERMATITIS.

SWALLOWED: SWALLOWING LARGE QUANTITIES CAUSES HEADACHES, NAUSEA, VOMITING, AND PERHAPS UNCONSCIOUSNESS. CAN ALSO CAUSE LIVER AND KIDNEY INJURY.

CHRONIC EFFECTS OF EXPOSURE: NO SPECIFIC INFORMATION AVAILABLE.

MEDICAL CONDITIONS GENERALLY AGGRAVATED BY EXPOSURE: PREEXISTING EYE OR SKIN DISORDERS MAY BE AGGRAVATED BY ACETONE EXPOSURE. ALSO, USE OF ALCOHOLIC BEVERAGES ENHANCES TOXIC EFFECTS.

TOXICITY DATA

ORAL: RAT LD50 = 9750 MG/KG

DERMAL: RABBIT LD50 = 20 G/KG

INHALATION: RAT LC50 = 16,000 PPM/4 HR

CARCINOGENICITY: THIS MATERIAL IS NOT CONSIDERED TO BE A CARCINOGEN BY THE NATIONAL TOXICOLOGY PROGRAM, THE INTERNATIONAL AGENCY FOR RESEARCH ON CANCER, OR THE OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION

OTHER DATA: INHALATION HUMAN TCLO = 500 PPM (EYE)

PERSONAL PROTECTION

VENTILATION: LOCAL MECHANICAL EXHAUST VENTILATION CAPABLE OF MAINTAINING EMISSIONS AT THE POINT OF USE BELOW THE PEL.

RESPIRATORY PROTECTION: IF USE CONDITIONS GENERATE VAPORS OR MISTS, WEAR A NIOSH-APPROVED RESPIRATOR APPROPRIATE FOR THOSE EMISSION LEVELS. APPROPRIATE RESPIRATORS MAY BE A FULL FACEPIECE OR A HALF MASK AIR-PURIFYING CARTRIDGE RESPIRATOR EQUIPPED FOR ORGANIC VAPORS/MISTS, A SELF-CONTAINED BREATHING APPARATUS IN THE PRESSURE DEMAND MODE, OR A SUPPLIED-AIR RESPIRATOR.

EYE PROTECTION: CHEMICAL GOGGLES UNLESS A FULL FACEPIECE RESPIRATOR IS ALSO WORN. IT IS GENERALLY RECOGNIZED THAT CONTACT LENSES SHOULD NOT BE WORN WHEN WORKING WITH CHEMICALS BECAUSE CONTACT LENSES MAY CONTRIBUTE TO THE SEVERITY OF AN EYE INJURY.

PROTECTIVE CLOTHING: LONG-SLEEVED SHIRT, TROUSERS, SAFETY SHOES, RUBBER GLOVES, AND RUBBER APRON.

OTHER PROTECTIVE MEASURES: AN EYEWASH AND SAFETY SHOWER SHOULD BE NEARBY AND READY FOR USE.

FIRE AND EXPLOSION INFORMATION

FLASH POINT, DEG F: 0
METHOD USED: TCC

FLAMMABLE LIMITS IN AIR, %
LOWER: 2 UPPER: 13

XTINGUISHING MEDIA: USE WATER SPRAY, DRY CHEMICAL, CO2, OR ALCOHOL JAM.

SPECIAL FIRE FIGHTING PROCEDURES: FIRE FIGHTERS SHOULD WEAR SELF-CONTAINED BREATHING APPARATUS AND FULL PROTECTIVE CLOTHING. USE WATER SPRAY TO COOL NEARBY CONTAINERS AND STRUCTURES EXPOSED TO FIRE.

UNUSUAL FIRE AND EXPLOSION HAZARDS: ACETONE IS EXTREMELY FLAMMMABLE. EXTINGUISH ALL NEARBY SOURCES OF IGNITION AVOID ACCUMULATION OF WATER OR ACETONE VAPORS BECAUSE AQUEOUS SOLUTIONS CONTAINING MORE THAN 2.5% ACETONE ARE FLAMMABLE.

HAZARDOUS REACTIVITY

STABILITY: STABLE POLYMERIZATION: WILL NOT OCCUR
CONDITIONS TO AVOID: HEAT, SPARKS, AND OPEN FLAMES.

MATERIALS TO AVOID: ACIDS, OXIDIZING MATERIALS, POTASSIUM T-BUTOXIDE, ALKALIS, AMINES, ALKANOLAMINES, AMMONIA, ALDEHYDES, AND CHLORINATED COMPOUNDS.

HAZARDOUS DECOMPOSITION PRODUCTS: MAY LIBERATE CARBON MONOXIDE, CARBON DIOXIDE, AND UNIDENTIFIED ORGANIC COMPOUNDS IN BLACK SMOKE.

SPILL, LEAK, AND DISPOSAL PROCEDURES

ACTION TO TAKE FOR SPILLS OR LEAKS: WEAR PROTECTIVE EQUIPMENT INCLUDING RUBBER BOOTS, RUBBER GLOVES, RUBBER APRON, AND A SELF-CONTAINED BREATHING APPARATUS IN THE PRESSURE DEMAND MODE OR A SUPPLIED-AIR RESPIRATOR. IF THE SPILL OR LEAK IS SMALL, A FULL FACEPIECE AIR-PURIFYING CARTRIDGE RESPIRATOR EQUIPPED FOR ORGANIC VAPORS MAY BE SATISFACTORY. IN ANY EVENT, ALWAYS WEAR EYE PROTECTION. EXTINGUISH ALL IGNITION SOURCES AND ENSURE THAT ALL HANDLING EQUIPMENT IS ELECTRICALLY GROUNDED. FOR SMALL SPILLS OR DRIPS, MOP OR WIPE UP AND DISPOSE OF IN DOT-APPROVED WASTE CONTAINERS. FOR LARGE SPILLS, CONTAIN BY DIKING WITH SOIL OR OTHER NON-COMBUSTIBLE ABSORBENT MATERIALS AND THEN PUMP INTO DOT-APPROVED WASTE CONTAINERS; OR ABSORB WITH NON-COMBUSTIBLE SORBENT MATERIAL, PLACE RESIDUE IN DOT-APPROVED WASTE CONTAINERS. KEEP OUT OF SEWERS, STORM DRAINS, SURFACE WATERS, AND SOIL.
COMPLY WITH ALL APPLICABLE GOVERNMENTAL REGULATIONS ON SPILL REPORTING, AND HANDLING AND DISPOSAL OF WASTE.

DISPOSAL METHODS: DISPOSE OF CONTAMINATED PRODUCT AND MATERIALS USED IN CLEANING UP SPILLS OR LEAKS IN A MANNER APPROVED FOR THIS MATERIAL. CONSULT APPROPRIATE FEDERAL, STATE AND LOCAL REGULATORY AGENCIES TO ASCERTAIN PROPER DISPOSAL PROCEDURES.
NOTE: EMPTY CONTAINERS CAN HAVE RESIDUES, GASES AND MISTS AND ARE SUBJECT TO PROPER WASTE DISPOSAL, AS ABOVE.

SPECIAL PRECAUTIONS

HANDLING AND STORAGE PRECAUTIONS: KEEP AWAY FROM HEAT, SPARKS, AND FLAMES. STORE IN A COOL, DRY, WELL-VENTILATED PLACE AWAY FROM INCOMPATIBLE MATERIALS. VENT CONTAINER FREQUENTLY, AND MORE OFTEN IN WARM WEATHER, TO RELIEVE PRESSURE. ELECTRICALLY GROUND ALL EQUIPMENT WHEN HANDLING THIS PRODUCT AND USE ONLY NON-SPARKING TOOLS. KEEP CONTAINER TIGHTLY CLOSED WHEN NOT IN USE. DO NOT USE PRESSURE TO EMPTY CONTAINER. WASH THOROUGHLY AFTER HANDLING. DO NOT GET IN EYES, ON SKIN, OR ON CLOTHING.

REPAIR AND MAINTENANCE PRECAUTIONS: DO NOT CUT, GRIND, WELD, OR DRILL ON OR NEAR THIS CONTAINER.

OTHER PRECAUTIONS: CONTAINERS, EVEN THOSE THAT HAVE BEEN EMPTIED, WILL RETAIN PRODUCT RESIDUE AND VAPORS. ALWAYS OBEY HAZARD WARNINGS AND HANDLE EMPTY CONTAINERS AS IF THEY WERE FULL.

FOR ADDITIONAL INFORMATION

JNTACT DOUGLAS EISNER, TECHNICAL DIRECTOR, VAN WATERS & ROGERS INC.
DURING BUSINESS HOURS, PACIFIC TIME (206)447-5911

OTHER REGULATORY INFORMATION

DO NOT DETACH THIS SECTION FROM THE MSDS AND BE SURE TO INCLUDE THIS SECTION WHEN COPYING THE MSDS.

THIS PRODUCT IS A TOXIC CHEMICAL SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF TITLE III OF THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT OF 1986 AND 40 CFR PART 372.

THIS PRODUCT CONTAINS THE FOLLOWING CHEMICAL(S) CONSIDERED BY THE STATE OF CALIFORNIA'S SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 (PROPOSITION 65) AS CAUSING CANCER OR REPRODUCTIVE TOXICITY AND FOR WHICH WARNINGS ARE NOW REQUIRED:

CHEMICAL	CAS NO.
BENZENE	71-43-2

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REVISION

08/87: REPORTED ADDITIONAL PERSONAL EXPOSURE LIMIT.

12/88: ADDED OTHER REGULATORY INFORMATION.

**** E N D O F M S D S ****

PROD: 04006155 01:57:20 16 JUN 1989 CUST: 21224602 INVOICE: 210745254

Material Safety Data Sheet
MSDS: 22577 - BENZENE
========== 2/20/92
atus: Current Revised: 10/23/90

Formula: C6H6 Part Number:
Specification: NOAA# 2577 Keyword:
Synonyms:
Stock Items:

Manufacturer
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Supplier
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Physical/Chemical Characteristics

Boiling Point .....:	176 F	@ 760 mm Hg
Melting Point .....:	42 F	
Freezing Point .....:		
Pour Point .....:		
Softening Point .....:		
Specific Gravity .....:	0.879	@ 68 Deg F
Vapor Pressure .....:	79.38	@ 70 Deg F
at Temperature ....:	70 F	
Vapor Density .....:		
Percent Volatiles ....:		
Evaporation Rate .....:		
pH .....:		
Molecular Weight .....:	78.11	
Viscosity .....:		
Solubility in Water ..:		

Odor/Appearance/Other Characteristics:

Fire and Explosion Data

Closed Cup Flash Pt. .:	12 F
Open Cup Flash Point .:	
Fire Point .....:	
Auto Ignition .....:	1097 F
Lower Explosion Limit :	1.3
Upper Explosion Limit :	7.9

Shipping Regulations
UN/NA Number: UN1114
DOT Hazard Class:
Shipping Label: FLAMMABLE LIQUID
Shipping Name:

epared
Preparer's Name & Title:
Preparation Date: 10/01/87

Component(s):
BENZENE
OSHA Pel:
ACGIH TLV: 10 ppm
STEL: 25 ppm
Percent of Product: CAS No.: 71432

Text Section(s)

Full Chemical Name

BENZENE
CAS number: 71432

Registry of Toxic Effects of Chemical Substances

CY1400000

Standard Transportation Commodities Code

4908110

List of synonyms for the chemical

BENZENE
\[6]ANNULENE
\BENZOL
\BENZOLE
\COAL NAPHTHA
\CYCLOHEXATRIENE
\PHENE
\PHENYL HYDRIDE
\PYROBENZOL
\PYROBENZOLE
\(6)ANNULENE
\BENZEEN (DUTCH)
\BENZEN (POLISH)
\BENZENE (ACGIH,DOT)
\BENZIN (OBS)
\BENZINE (OBS)
\BENZOL (DOT)
\BENZOLENE
\BENZOLO (ITALIAN)
\BICARBURET OF HYDROGEN
\CARBON OIL

\FENZEN (CZECH)
\MINERAL NAPHTHA
\MOTOR BENZOL
\NCI-C55276
\NITRATION BENZENE
\RCRA WASTE NUMBER U019
\UN 1114 (DOT)

DOT label

FLAMMABLE LIQUID

NFPA

NFPA rating for Health Hazard --
2
NFPA rating for Flammability Hazard --
3
NFPA rating for Reactivity Hazard --
0

General description of a chemical

Benzene is a clear colorless liquid with a characteristic aromatic odor. It is used to make other chemicals, as a solvent, and as a gasoline additive. It has a flash point of 12 deg F., and solidifies at 42 deg F. It is lighter than water and insoluble in water. Its vapors are heavier than air. ((C)AAR, 1986)

Fire and Explosion Hazards Information

Fire and explosion hazards --
FLAMMABLE. Flashback along vapor trail may occur. Vapor may explode if ignited in an enclosed area. Vapor is heavier than air and may travel considerable distance to a source of ignition and flash back. (USCG, 1985)
Fire fighting techniques --
Do not extinguish fire unless flow can be stopped. Use water in flooding quantities as fog. Solid streams of water may spread fire. Cool all affected containers with flooding quantities of water. Apply water from as far a distance as possible. Use foam, carbon dioxide or dry chemical. ((C)AAR, 1986)

Protective clothing recommendations

Avoid breathing vapors. Keep upwind. Wear boots, protective gloves, and goggles. Do not handle broken packages without protective equipment. Wash away any material which may have contacted the body with copious amounts of water or soap and water. ((C)AAR, 1986)

Compatibility

Compatibility with Butyl Rubber --
Poor Resistance/Good Data.
Compatibility with chlorinated natural rubber --
Poor Resistance/Limited Data.
Compatibility with chlorinated polyehtylene --
Poor Resistance/Limited Data.
Compatibility with ethyl vinyl (14%)/Polyethylene (86%) coated fabric --
Poor Resistance/Limited Data.
Compatibility with Teflon --
Poor Resistance/Good Data.
Compatibility with nitrile/butadiene coated fabric --
Good Resistance/Limited Data.
Compatibility with neoprene --
Poor Resistance/Good Data.
Compatibility with neoprene/natural rubber blend --
Poor Resistance/Good Data.
Compatibility with neoprene/SBR coated nylon or cotton --
Poor Resistance/Limited Data.
Compatibility with nitrile coated fabric --
Poor Resistance/Good Data.
Compatibility with nitrile/PVC coated fabric --
Good Resistance/Good Data.
Compatibility with polyethylene --
Poor Resistance/Good Data.
Compatibility with polyurethane --
Poor Resistance/Good Data.
Compatibility with polyvinyl alcohol --
Poor Resistance/Good Data.
Compatibility with polyvinyl chloride --
Poor Resistance/Good Data.
Compatibility with natural rubber --
Poor Resistance/Good Data.
Compatibility with Saranex coated tyvex --
Poor Resistance/Limited Data.
Compatibility with styrene/butadiene coated fabric --
Poor Resistance/Good Data.
Compatibility with Viton --
Good Resistance/Limited Data.

Evacuation information

Isolate for 1/2 mile in all directions if tank car or truck is involved in fire. (DOT, 1984)

Non-Fire response information

Keep sparks, flames, and other sources of ignition away. Keep material out of water sources and sewers. Build dikes to contain flow as necessary. Attempt to stop leak if without hazard. Use water spray to knock-down vapors. Land spill: Dig a pit, pond, lagoon, holding area to contain liquid or solid material. Dike surface flow using soil, sand bags, foamed polyurethane, or foamed concrete. Absorb bulk liquid with fly ash, cement powder, sawdust, or commercial sorbents. Apply fluorocarbon-water foam to diminish vapor and fire hazard. Water spill: Use natural barriers or oil spill control booms to limit spill motion. Use surface active agent (e.g. detergent, soaps, alcohols) to compress and thicken spilled material. Inject "universal" gelling agent to solidify encircled spill and increase effectiveness of booms. If dissolved, apply activated carbon at ten times the spilled amount in region of 10 ppm or greater concentration. Remove trapped material with suction hoses. Use mechanical dredges or lifts to remove immobilized masses of pollutants and precipitates. Air spill: Apply water spray or mist to knock down vapors. ((C)AAR, 1986)

Health hazard information

VAPOR: Irritating to eyes, nose and throat. If inhaled, will cause headache, difficult breathing, or loss of consciousness. LIQUID: Irritating to skin and eyes. Harmful if swallowed. (USCG, 1985)

First aid information

If this chemical comes in contact with the eyes, immediately wash the eyes with large amounts of water, occasionally lifting the lower and upper lids. Get medical attention immediately. Contact lenses should not be worn when working with this chemical. If this chemical comes in contact with the skin, promptly wash the contaminated skin with soap and water. If this chemical penetrates through the clothing, promptly remove the clothing and wash the skin with soap and water. Get medical attention promptly. If a person breathes in large amounts of this chemical, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible. If this chemical has been swallowed, get medical attention immediately. (NIOSH, 1987)

Fire and Explosion Data

Flash point of chemical --
12 Deg F c.c. (USCG, 1985)
Lower explosive limit --
1.3 % (USCG, 1985)
Upper explosive limit --
7.9 % (USCG, 1985)
Auto-ignition temperature --
1097 Deg F (USCG, 1985)

Physical / Chemical Characteristics

Melting point --
42 Deg F (USCG, 1985)
Vapor pressure --
79.38 mm Hg @ 70 Deg F (USCG, 1985)
Specific gravity of vapor form --
2.7 (USCG, 1985)
Specific gravity of liquid form --
0.879 @ 68 Deg F (USCG, 1985)
Boiling point --
176 Deg F @ 760 mm Hg (USCG, 1985)
Molecular weight --
78.11 (USCG, 1985)

Exposure Limits

NIOSH Immediately Dangerous to Life and Health value --
Not applicable, potential human carcinogen. (NIOSH, 1987)
Time Weighted Average of the Threshold Limit Value --
10 ppm ((C)ACGIH, 1986)
Short Term (15 minute) Exposure limit of the Threshold Limit Value --
25 ppm ((C)ACGIH, 1986)

End of MSDS

Material Safety Data Sheet
MSDS: 22828 - CARBON TETRACHLORIDE
========== 3/12/92
Status: Current Revised: 10/23/90

Formula: CCl4 Part Number:
Specification: NOAA# 2828 Keyword:
Synonyms:
Stock Items:

Manufacturer
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Supplier
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Physical/Chemical Characteristics

Boiling Point .....:	170 F	@ 760 mm Hg
Melting Point .....:	-9.4 F	
Freezing Point .....:		
Pour Point .....:		
Softening Point .....:		
Specific Gravity .....:	1.59	@ 68 Deg F
Vapor Pressure .....:	96.91	@ 70 Deg F
at Temperature ....:	70 F	
Vapor Density .....:		
Percent Volatiles ....:		
Evaporation Rate .....:		
pH .....:		
Molecular Weight .....:	153.83	
Viscosity .....:		
Solubility in Water ..:		

Odor/Appearance/Other Characteristics:

Fire and Explosion Data

Closed Cup Flash Pt. .:	NA	Not flammable.
Open Cup Flash Point .:		
Fire Point .....:		
Auto Ignition .....:	NA	Not flammable.
Lower Explosion Limit :	NA	Not flammable.
Upper Explosion Limit :	NA	Not flammable.

Shipping Regulations
UN/NA Number: UN1846
DOT Hazard Class:
Shipping Label: ORM-A
Shipping Name:

pared
Preparer's Name & Title:
Preparation Date: 10/01/87

Component(s):
CARBON TETRACHLORIDE
OSHA Pel:
ACGIH TLV: 5 ppm
STEL:
Percent of Product: CAS No.: 56235

Text Section(s)

Full Chemical Name

CARBON TETRACHLORIDE
CAS number: 56235

Registry of Toxic Effects of Chemical Substances

FG4900000

Standard Transportation Commodities Code

4940320

List of synonyms for the chemical

METHANE, TETRACHLORO-
\BENZINOFORM
\CARBONA
\CARBON CHLORIDE (CCL4)
\CARBON TETRACHLORIDE
\FLUKOIDS
\NECATORINA
\PERCHLOROMETHANE
\R 10
\R 10 (REFRIGERANT)
\TETRACHLOROMETHANE
\TETRAFINOL
\TETRAFORM
\TETRASOL
\UNIVERM
\VERMOESTRICID
\CARBON CHLORIDE
\CARBON TET
\CARBON TETRACHLORIDE (ACGIH,DOT)
\CZTEROCHLOREK WEGLA (POLISH)
\ENT 4,705

\FASCIOLIN
\METHANE TETRACHLORIDE
\NECATORINE
\RCRA WASTE NUMBER U211
\TETRACHLOORKOOLSTOF (DUTCH)
\TETRACHLOORMETAAN
\TETRACHLORKOHLENSTOFF, TETRA (GERMAN)
\TETRACHLORMETHAN (GERMAN)
\TETRACHLOROCARBON
\TETRACHLORURE DE CARBONE (FRENCH)
\TETRACLOROMETANO (ITALIAN)
\TETRACLORURO DI CARBONIO (ITALIAN)
\UN 1846 (DOT)

DOT label

ORM-A

NFPA

NFPA rating for Health Hazard --
3
NFPA rating for Flammability Hazard --
0
NFPA rating for Reactivity Hazard --
0

General description of a chemical

Carbon tetrachloride is a clear colorless heavy liquid with a characteristic odor. It is used as a solvent, in the manufacture of other chemicals, as an agricultural fumigant, and for many other uses. It is heavier than water and insoluble in water. It is non-combustible. It can cause illness by inhalation, skin absorption and/or ingestion. ((C)AAR, 1986)

Fire and Explosion Hazards Information

Fire and explosion hazards --
Not flammable. POISONOUS AND IRRITATING GASES ARE PRODUCED WHEN HEATED. Forms poisonous phosgene gas when exposed to open flames. Decomposes to form chlorine and phosgene. (USCG, 1985)
Fire fighting techniques --
Extinguish fire using agent suitable for type of surrounding fire (material itself does not burn or burns with difficulty). ((C)AAR, 1986)

Protective clothing recommendations

Keep upwind. Wear boots, protective gloves, and goggles. Avoid breathing vapors or dusts. Wash away any material which may have contacted the body with copious amounts of water or soap and water. ((C)AAR, 1986)

Compatibility

Compatibility with Butyl Rubber --
Poor Resistance/Good Data.
Compatibility with chlorinated polyehtylene --
Poor Resistance/Limited Data.
Compatibility with nitrile/butadiene coated fabric --
Good Resistance/Limited Data.
Compatibility with neoprene --
Poor Resistance/Good Data.
Compatibility with neoprene/natural rubber blend --
Poor Resistance/Good Data.
Compatibility with neoprene/SBR coated nylon or cotton --
Poor Resistance/Limited Data.
Compatibility with nitrile coated fabric --
Good Resistance/Good Data.
Compatibility with nitrile/PVC coated fabric --
Good Resistance/Limited Data.
Compatibility with polyethylene --
Poor Resistance/Good Data.
Compatibility with polyurethane --
Poor Resistance/Limited Data.
Compatibility with polyvinyl alcohol --
Good Resistance/Good Data.
Compatibility with polyvinyl chloride --
Poor Resistance/Good Data.
Compatibility with natural rubber --
Poor Resistance/Good Data.
Compatibility with styrene/butadiene coated fabric --
Poor Resistance/Good Data.
Compatibility with Viton --
Good Resistance/Limited Data.

Non-Fire response information

Keep material out of water sources and sewers. Build dikes to contain flow as necessary. Land spill: Dig a pit, pond, lagoon, holding area to contain liquid or solid material. Dike surface flow using soil, sand bags, foamed polyurethane, or foamed concrete. Absorb bulk liquid with fly ash or cement powder. Apply "universal" gelling agent to immobilize spill. Water spill: Use natural deep water pockets, excavated lagoons, or sand bag barriers to trap material at bottom. Remove trapped material with suction hoses. If dissolved, apply activated carbon at ten times the spilled amount in region of 10 ppm or greater concentration. Use mechanical dredges or lifts to remove immobilized masses of pollutants and precipitates. Air spill: Apply water spray or mist to knock down vapors. Vapor knockdown water is corrosive or toxic and should be diked for containment. Thermal decomposition to phosgene can occur. ((C)AAR, 1986)

Health hazard information

VAPOR: POISONOUS IF INHALED. Irritating to eyes Move to fresh air.
LIQUID: POISONOUS IF SWALLOWED. Irritating to skin and eyes. (USCG, 1985)

First aid information

If this chemical comes in contact with the eyes, immediately wash the eyes with large amounts of water, occasionally lifting the lower and upper lids. Get medical attention immediately. Contact lenses should not be worn when working with this chemical. If this chemical comes in contact with the skin, immediately wash the contaminated skin with soap and water. If this chemical penetrates through the clothing, immediately remove the clothing, wash the skin with soap and water, get medical attention promptly. If a person breathes in large amounts of this chemical, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible. If this chemical has been swallowed, get medical attention immediately. (NIOSH, 1987)

Fire and Explosion Data

Flash point of chemical --
    Not Applicable. Not flammable. (USCG, 1985)
Lower explosive limit --
    Not Applicable. Not flammable. (USCG, 1985)
Upper explosive limit --
    Not Applicable. Not flammable. (USCG, 1985)
Auto-ignition temperature --
    Not Applicable. Not flammable. (USCG, 1985)

Physical / Chemical Characteristics

Melting point --
-9.4 Deg F (USCG, 1985)
Vapor pressure --
96.91 mm Hg @ 70 Deg F (USCG, 1985)
Specific gravity of vapor form --
5.3 (USCG, 1985)
Specific gravity of liquid form --
1.59 @ 68 Deg F (USCG, 1985)
Boiling point --
170 Deg F @ 760 mm Hg (USCG, 1985)
Molecular weight --
153.83 (USCG, 1985)

Exposure Limits

NIOSH Immediately Dangerous to Life and Health value --
Not applicable, potential human carcinogen. (NIOSH, 1987)
Time Weighted Average of the Threshold Limit Value --
5 ppm Skin. ((C)ACGIH, 1986)

COMPOUND NAME CHLOROBENZENE

CAS #	108-90-7		
USEPA HAZ WASTE CODE	U037		
IDLH	2400 PPM		
TLV-TWA	10 PPM	TLV-STEL	TLV-C
VAPOR PRESSURE (mmHg) @ 20 °C	11.8 @ 25 °C		
NFPA-H[1]	2	NFPA-F[2]	3
NFPA-R[3]	0	NFPA-S[4]	-
US DOT CLASSIFICATION	3- FLAMMABLE LIQUID		
HAZARDOUS DECOMPOSITION PRODUCTS	HYDROGEN CHLORIDE, PHOSGENE, CARBON MONOXIDE		
OTHER			

[1] NFPA HEALTH [2] NFPA FIRE [3] NFPA REACTIVITY [4] NFPA SPECIFIC HAZARD U=UNKNOWN

Material Safety Data Sheet

Genium Publishing Corporation
1145 Catalyn Street, Schenectady, NY 12303
(518) 377-8854
From Genium's collection, to be used as reference

Product: CHLOROBENZENE

MSDS No: Genium / 366
Revision: A
Date: November, 1982

SECTION I. MATERIAL IDENTIFICATION

Trade/Material Name: CHLOROBENZENE

Other Designations: Chlorobenzol, Monochlorobenzene, Phenyl Chloride, C_6H_5Cl

CAS: 000 108 907

Available from several suppliers.

SECTION II. INGREDIENTS AND HAZARDS

Ingredient Name:	Percent:	Exposure Limits:
Chlorobenzene	ca 100	8-hr TWA 75 ppm or 350 mg/m³*
		Rat, Oral LD50 2910 mg/kg
		Mouse, Inhalation LCLo 15 gm/m³

* Current OSHA PEL and ACGIH (1982) TLV. Long term bioassay was underway at NCI in 1980.

SECTION III. PHYSICAL DATA

Appearance & Odor: A clear, colorless, volatile liquid with a faint, almond-like odor.

Threshold odor conc: 100% recognition, 0.21 ppm. Good warning properties.

Boiling point: 132xC, 1 atm
Vapor pressure: 11.8 @ 25xC, mm Hg
Water solubility (%): 0.049 @ 25xC, g/100g H_2O
Vapor density (air=1): 3.9
Evaporation rate: 1.0 (n-BuAc=1)
Specific gravity (H_2O=1): 1.11
Melting point: ca -45xC
% volatile by volume: ca 100
Molecular weight: 112.56

Log Octanal/water Partition: 2.83

SECTION IV. FIRE AND EXPLOSION DATA

Flash Point (method): 29xC (84xF) (TCC) **Limits: LEL %:** 1.3% **UEL %:** *

Extinguishing Media: CO_2, dry chemical, or foam. A water spray can be used to control small fires or cool fire-exposed containers. A layer of water can be used to blanket chlorobenzene and may be useful for extinguishing fire in an open tank.

Autoignition Temp: 638xC (1180xF)

Unusual fire or explosion hazards: Vapors of this material may flow along surfaces for a considerable distance, reach an ignition source, and flash back. A dangerous fire hazard when exposed to heat or flames.

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FIRE AND EXPLOSION DATA continued from page 1

Special fire-fighting procedures: Firefighters should use eye protection and self-contained breathing apparatus in fighting fires in which this material is involved.

* 7.1%; 9.6% @ 150xC

SECTION V. REACTIVITY DATA

Material is stable in closed containers at room temperature under normal storage and handling conditions. Hazardous polymerization cannot occur

Chemical incompatibilities: It is incompatible with oxidizing agents. Chlorobenzene can react violently with dimethyl sulfoxide. Silver perchlorate will form a solvated salt with chlorobenzene which is shock sensitive (explosion).

Hazardous decomposition Products: Thermal-oxidative degradation products can include soot, hydrogen chloride, phosgene, and carbon monoxide.

SECTION VI. HEALTH HAZARD INFORMATION

Summary of risks: Chlorobenzene is a fairly strong narcotic and can cause CNS depression. Overexposure is irritating to the eyes, nasal passages, and upper respiratory tract. It is moderately toxic by inhaltion or ingestion and can be absorbed slowly through the skin. Short exposures to liquid may cause skin irritation and defatting, while prolonged or repeated skin contact may result in dermatitis or skin burns.
Repeated inhalation exposures to animals at 1,000 ppm over a period of 44 days resulted in lung, liver, and kidney changes; at 475 ppm slight liver changes were observed; no abnormal effects noted at 200 ppm.

Acute effects: Symptoms to be expected from acute exposure are headache, dizziness, drowsiness, cyanosis, spastic contractions of extremities, and loss of consciousness, depending on conc. and time of exposure.

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HEALTH HAZARD INFORMATION continued from page 2

First aid:

Eye contact: Flush thoroughly with running water for 15 minutes, including under eyelids.

Skin contact: Remove contaminated clothing. Wash area promptly with soap and water.

Inhalation: Remove to fresh air. Restore and/or support breathing as required.

Ingestion: Contact physician and/or transport for gastric lavage.

Seek prompt medical help for treatment, observation and support after first aid. Preplacement and periodic medical examinations should emphasize skin, liver, lung, and kidney disorders. Those with such problems may be at an increased risk from exposure.

SECTION VII. SPILL, LEAK AND DISPOSAL PROCEDURES

Spill / Leak procedures: Make prior plans to handle emergencies. Suppliers can be helpful.
Eliminate ignition sources; notify safety personnel. Provide ventilation (explosion proof). Clean up workers need protection against inhalation of vapors and contact with liquid. Collect spill with absorbent solid, such as paper or sawdust, or as a liquid and place in sealed metal container for disposal. Use non-sparking tools.

Waste management / Disposal: Dispose of scrap by burning in an approved incinerator with a scrubber, or dispose of through a licensed waste disposal company. Follow Federal, State and Local regulations.

AQUATIC TOXICITY TLm 96: 100-1 ppm
EPA (RCRA) HW No. U037 (40CFR261)
EPA (CWA) RO 100 lb (40 CFR 117)

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Product: CHLOROBENZENE

MSDS No: Genium / 366
Revision: A
Date: November, 1982

SECTION VIII. SPECIAL PROTECTION INFORMATION

Personal protective equipment:

Goggles: Use chemical safety goggles where splashing is possible.

Gloves: Use impervious (VITON is best; neoprene, "fair") gloves.

Respirator: Use a chemical cartridge respirator with a full facepiece and an organic vapor cartridge for vapor conc. <1000 ppm. A self-contained breathing apparatus with full facepiece is suitable to use up to 2400 ppm.

Other: Use impervious (VITON is best, neoprene, "fair") aprons, protective clothing, etc.

Workplace considerations:

Ventilation: Provide adequate general and local exhaust ventilation (explosion-proof equipment!) to meet TLV requirements.

Safety stations:
Provide an eyewash station and safety shower in area of use and handling.

Clothing soiled with liquid to be removed promptly and laundered before reuse.

SECTION IX. SPECIAL PRECAUTIONS

Storage segregation: Store in tightly closed containers in a well-ventilated, fire-resistant area away from heat, sources of ignition, and oxidizing agents. Outside or detached area preferred. Storage and handling must be suitable for an OSHA Class IC Flammable Liquid. Protect containers from physical damage.

Engineering controls: Ground and bond containers and equipment for transfers to avoid static sparks. Use non-sparking tools. Electrical services must meet code. Use safety cans for small amounts.

Other precautions: Avoid breathing vapors! Avoid contact with liquid. Do not ingest.

LABEL: FLAMMABLE LIQUID

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Product: CHLOROBENZENE

MSDS No: Genium / 366
Revision: A
Date: November, 1982

SPECIAL PRECAUTIONS continued from page 4

DOT Class: FLAMMABLE LIQUID **UN Register:** UN1134
Data source code(s): 2-12, 14, 16, 23, 25-27, 31, 34, 37, 38, 45-47, 49. N

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OHS04770

OHS04770

SECTION 1 CHEMICAL PRODUCTS & COMPANY IDENTIFICATION

OCCUPATIONAL HEALTH SERVICES, INC.
11 WEST 42ND STREET, 12TH FLOOR
NEW YORK, NEW YORK 10036
1-800-445-MSDS (1-800-445-6737) OR
1-212-789-3535

FOR EMERGENCY SOURCE INFORMATION
CONTACT: 1-615-366-2000

CAS NUMBER: 67-66-3
RTECS NUMBER: FS9100000

SUBSTANCE: CHLOROFORM

TRADE NAMES/SYNONYMS:
TRICHLOROMETHANE; METHANE TRICHLORIDE; R 20; FREON 20; METHANE, TRICHLORO-; METHYL TRICHLORIDE; TRICHLOROFORM; R 20 (REFRIGERANT); METHENYL TRICHLORIDE; RCRA U044; STCC 4940310; UN 1888; CHCL3; OHS04770

CHEMICAL FAMILY:
Halogen compound, aliphatic

CREATION DATE: 10/01/84 REVISION DATE: 10/06/93

SECTION 2 COMPOSITION/INFORMATION ON INGREDIENTS

COMPONENT : CHLOROFORM
CAS NUMBER: 67-66-3
PERCENTAGE: >99

OTHER CONTAMINANTS: MAY CONTAIN TRACES OF A STABILIZER.

SECTION 3 HAZARDS IDENTIFICATION

CERCLA RATINGS (SCALE 0-3): HEALTH=3 FIRE=0 REACTIVITY=0 PERSISTENCE=3
NFPA RATINGS (SCALE 0-4): HEALTH=2 FIRE=0 REACTIVITY=0

EMERGENCY OVERVIEW:
CHLOROFORM IS A CLEAR LIQUID WITH A SWEET ODOR. IF YOU CAN SMELL IT YOU MAY BE EXCEEDING THE EXPOSURE LIMIT.
Suspect cancer hazard (contains material which can cause cancer in animals). Risk of cancer depends on duration and level of exposure. May cause liver damage. May damage kidneys. May affect the central nervous system. Causes respiratory tract, skin and eye irritation. No known fire or reactivity hazard.
Avoid breathing vapor or mist. Avoid contact with eyes, skin and clothing. Keep container tightly closed. Wash thoroughly after handling. Use only with adequate ventilation.

POTENTIAL HEALTH EFFECTS:

NHALATION:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include drunkeness, drooling, nausea, vomiting, low blood pressure, irregular heartbeat, headache, weakness, fainting, disorientation, excitation or drowsiness, numbness, dilated pupils, liver and kidney damage, convulsions, unconsciousness and coma.
LONG TERM EFFECTS: In addition to effects from short term exposure, thirst, dry mouth, lack of appetite, digestive disorders, anemia, confusion, tingling sensation, twitching, loss of memory, blurred vision and liver enlargement may occur.

SKIN CONTACT:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include weight loss.
LONG TERM EFFECTS: Same effects as short term exposure.

EYE CONTACT:
SHORT TERM EFFECTS: May cause irritation. Additional effects may include tearing, numbness and spastic winking.
LONG TERM EFFECTS: Same effects as short term exposure.

INGESTION:
SHORT TERM EFFECTS: May cause drunkeness, liver damage, kidney damage, lack of appetite, nausea, vomiting, diarrhea, blood in the urine, difficulty breathing, low blood pressure, dilated pupils, bluish skin color, lung damage and unconsciousness.
LONG TERM EFFECTS: In addition to effects from short term exposure, liver and kidney damage may occur. May also cause reproductive effects and cancer.

CARCINOGEN STATUS:
OSHA: N
NTP: Y
IARC: Y

SECTION 4 FIRST AID MEASURES

INHALATION:
FIRST AID- Remove from exposure area to fresh air immediately. If breathing has stopped, perform artificial respiration. Keep person warm and at rest. Treat symptomatically and supportively. Get medical attention immediately.

SKIN CONTACT:
FIRST AID- Remove contaminated clothing and shoes immediately. Wash affected area with soap or mild detergent and large amounts of water until no evidence of chemical remains (approximately 15-20 minutes). Get medical attention immediately.

EYE CONTACT:
FIRST AID- Wash eyes immediately with large amounts of water or normal saline, occasionally lifting upper and lower lids, until no evidence of chemical remains (approximately 15-20 minutes). Get medical attention immediately.

INGESTION:
FIRST AID- Treat symptomatically and supportively. Get medical attention immediately. If vomiting occurs, keep head lower than hips to prevent

aspiration.

NOTE TO PHYSICIAN
ANTIDOTE:
No specific antidote. Treat symptomatically and supportively.

SECTION 5 FIRE FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:
Negligible fire hazard when exposed to heat or flame.

EXTINGUISHING MEDIA:
Dry chemical, water spray or regular foam
(1990 Emergency Response Guidebook, DOT P 5800.5).

For larger fires, use water spray, fog or regular foam
(1990 Emergency Response Guidebook, DOT P 5800.5).

FIREFIGHTING:
Move container from fire area if you can do it without risk. Fight fire from maximum distance. Stay away from ends of tanks. Dike fire-control water for later disposal; do not scatter the material (1990 Emergency Response Guidebook, DOT P 5800.5, Guide Page 55).

Extinguish using agents suitable for type of fire. Avoid breathing vapors or dusts, keep upwind.

AUTOIGNITION: >1832 F (>1000 C)

HAZARDOUS COMBUSTION PRODUCTS:
CHLOROFORM:
Thermal decomposition may release toxic or corrosive vapors, including oxides of chlorine and carbon, phosgene, chlorine gas and hydrogen chloride.

SECTION 6 ACCIDENTAL RELEASE MEASURES

OCCUPATIONAL SPILL:
Do not touch spilled material. Stop leak if you can do it without risk. Use water spray to reduce vapors. For small spills, take up with sand or other absorbent material and place into containers for later disposal. For small dry spills, with a clean shovel place material into clean, dry containers and cover. Move containers from spill area. For larger spills, dike far ahead of spill for later disposal. Keep unnecessary people away. Isolate hazard area and deny entry. Ventilate closed spaces before entering.

Reportable Quantity (RQ):
The Superfund Amendments and Reauthorization Act (SARA) Section 304 requires that a release equal to or greater than the reportable quantity established for that substance be immediately reported to the local emergency planning committee and the state emergency response commission (40 CFR 355.40). If the release of this substance is reportable under CERCLA Section 103, the National Response Center must be notified immediately at (800) 424-8802 or

202) 426-2675 in the metropolitan Washington, D.C. area (40 CFR 302.6).

SOIL SPILL:
Dig a holding area such as a pit, pond or lagoon to contain spill and dike surface flow using barrier of soil, sandbags, foamed polyurethane or foamed concrete. Absorb liquid mass with fly ash or cement powder.

Immobilize spill with universal gelling agent.

AIR SPILL:
Combustion products include corrosive or toxic vapors.

WATER SPILL:
Trap spilled material at bottom in deep water pockets, excavated holding areas or within sand bag barriers.

Use suction hoses to remove trapped spill material.

Use mechanical dredges or lifts to extract immobilized masses of pollution and precipitates.

If dissolved, at a concentration of 10 ppm or greater, apply activated carbon at ten times the amount that has been spilled.

The California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65) prohibits contaminating any known source of drinking water with substances known to cause cancer and/or reproductive toxicity.

SECTION 7 HANDLING AND STORAGE

Observe all federal, state and local regulations when storing this substance.

Threshold Planning Quantity (TPQ):
The Superfund Amendments and Reauthorization Act (SARA) Section 302 requires that each facility where any extremely hazardous substance is present in a quantity equal to or greater than the TPQ established for that substance notify the state emergency response commission for the state in which it is located. Section 303 of SARA requires these facilities to participate in local emergency response planning (40 CFR 355.30).

Store in a cool, dry, well-ventilated location. Separate from strong alkalis (NFPA 49, Hazardous Chemicals Data, 1975).

Store away from incompatible substances.

Keep container tightly closed. Protect from exposure to air or light.

SECTION 8 EXPOSURE CONTROLS/PERSONAL PROTECTION

EXPOSURE LIMITS:
CHLOROFORM:
2 ppm (9.78 mg/m3) OSHA TWA

10 ppm (49 mg/m3) ACGIH TWA
ACGIH A2-Suspected Human Carcinogen.
2 ppm (9.78 mg/m3) NIOSH recommended 60 minute STEL
10 ppm (49 mg/m3) DFG MAK TWA;
20 ppm (98 mg/m3) DFG MAK 30 minute peak, average value, 4 times/shift

Measurement method: Charcoal tube; carbon disulfide; gas chromatography with flame ionization detection; (NIOSH Vol. III # 1003, Halogenated Hydrocarbons).

10,000 pounds SARA Section 302 Threshold Planning Quantity
5000 pounds SARA Section 304 Reportable Quantity
10 pounds CERCLA Section 103 Reportable Quantity
Subject to SARA Section 313 Annual Toxic Chemical Release Reporting
Subject to California Proposition 65 cancer and/or reproductive toxicity warning and release requirements- (October 1, 1987)

OSHA revoked the final rule limits of January 19, 1989 in response to the 11th Circuit Court of Appeals decision (AFL-CIO v. OSHA) effective June 30, 1993. See 29 CFR 1910.1000 (58 FR 35338)

VENTILATION:
Provide local exhaust or process enclosure ventilation to meet published exposure limits.

EYE PROTECTION:
Employee must wear splash-proof or dust-resistant safety goggles and a faceshield to prevent contact with this substance.

Emergency wash facilities:
Where there is any possibility that an employee's eyes and/or skin may be exposed to this substance, the employer should provide an eye wash fountain and quick drench shower within the immediate work area for emergency use.

CLOTHING:
Employee must wear appropriate protective (impervious) clothing and equipment to prevent repeated or prolonged skin contact with this substance.

GLOVES:
Employee must wear appropriate protective gloves to prevent contact with this substance.

RESPIRATOR:
The following respirators and maximum use concentrations are recommendations by the U.S. Department of Health and Human Services, NIOSH pocket guide to chemical hazards; NIOSH criteria documents or by the U.S. Department of Labor, 29 CFR 1910 Subpart Z.
The specific respirator selected must be based on contamination levels found in the work place, must not exceed the working limits of the respirator and be jointly approved by the National Institute for Occupational Safety and Health and the Mine Safety and Health Administration (NIOSH-MSHA).

CHLOROFORM:

.t any detectable concentration:
Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive pressure-mode.
Any supplied-air respirator with a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

Escape:
Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister.
Any appropriate escape-type, self-contained breathing apparatus.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS

Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

DESCRIPTION: Clear, colorless, heavy, volatile liquid with a sweet pleasant ethereal taste and odor.
MOLECULAR WEIGHT: 119.38
MOLECULAR FORMULA: C-H-CL3
BOILING POINT: 143 F (62 C)
MELTING POINT: -82 F (-64 C)
VAPOR PRESSURE: 160 mmHg @ 20 C
VAPOR DENSITY: 4.12
SPECIFIC GRAVITY: 1.4832
WATER SOLUBILITY: 0.82% @ 20 C
VOLATILITY: 100%
ODOR THRESHOLD: 200 ppm
EVAPORATION RATE: (butyl acetate=1) 11.6
SOLVENT SOLUBILITY: Soluble in alcohol, ether, acetone, benzene, ligroin, solvent naphtha, petroleum ether, carbon tetrachloride, carbon disulfide, oils, other organic solvents.

VISCOSITY: 56.3 cP @ 20 C

SECTION 10 STABILITY AND REACTIVITY

REACTIVITY:
Stable under normal temperatures and pressures.

CONDITIONS TO AVOID:
May burn but does not ignite readily. Containers may explode in heat of fire.

NCOMPATIBILITIES:
CHLOROFORM:
ALUMINUM (POWDERED): Explosion on contact.
BIS(DIMETHYLAMINO)DIMETHYLSTANNANE: Explosion when heated.
DINITROGEN TETRAOXIDE: Explosive mixture.
DISILANE: Vigorous incandescent reaction.
FLUORINE: Explosive reaction.
KETONES + ALKALIES: Vigorous exothermic reaction.
LITHIUM: Forms shock-sensitive mixture.
MAGNESIUM (POWDER): Explodes on contact.
METALS + WATER: May be attacked.
METHANOL + ALKALIES: Exothermic reaction.
NITROMETHANE: Forms explosive mixture.
PERCHLORIC ACID + PHOSPHOROUS PENTOXIDE: Violent explosion.
PLASTICS, RUBBER, COATINGS: May be attacked.
POTASSIUM: Explosive reaction.
POTASSIUM TERT-BUTOXIDE (VAPOR): Ignites on contact.
SODIUM: Explosive reaction.
SODIUM METHOXIDE: Incompatible.
TRIISOPROPYLPHOSPHINE: Vigorous reaction.

HAZARDOUS DECOMPOSITION:
CHLOROFORM:
Thermal decomposition may release toxic or corrosive vapors, including oxides of chlorine and carbon, phosgene, chlorine gas and hydrogen chloride.

POLYMERIZATION:
azardous polymerization has not been reported to occur under normal temperatures and pressures.

SECTION 11 TOXICOLOGY INFORMATION

CHLOROFORM:
IRRITATION DATA: 10 mg/24 hours open skin-rabbit mild; 500 mg/24 hours skin-rabbit mild; 148 mg eye-rabbit; 20 mg/24 hours eye-rabbit moderate.
TOXICITY DATA: 25,000 ppm/5 minutes inhalation-human LCLo; 10 mg/m3/1 year inhalation-human TCLo; 5000 mg/m3/7 minutes inhalation-human TCLo; 47,702 mg/m3/4 hours inhalation-rat LC50; 50 ppm/7 hours/26 weeks intermittent inhalation-rat TCLo; 28 gm/m3 inhalation-mouse LCLo; 59 gm/m3 inhalation-rabbit LCLo; 35 gm/m3/4 hours inhalation-cat LCLo; 100 gm/m3 inhalation-dog LCLo; 20,000 ppm/2 hours inhalation-guinea pig LCLo; 25 ppm/7 hours/26 weeks intermittent inhalation-guinea-pig TCLo; 25,000 ppm/5 minutes inhalation-mammal LCLo; >20 gm/kg skin-rabbit LD50; >4000 mg/kg skin-rabbit LD50 (Dow MSDS); 908 mg/kg oral-rat LD50; 36 mg/kg oral-mouse LD50; 1000 mg/kg oral-dog LDLo; 500 mg/kg oral-rabbit LDLo; 820 mg/kg oral-guinea pig LD50; 704 mg/kg subcutaneous-mouse LD50; 800 mg/kg subcutaneous-rabbit LDLo; 75 mg/kg intravenous-dog LDLo; 894 mg/kg intraperitoneal-rat LD50; 623 mg/kg intraperitoneal-mouse LD50; 1000 mg/kg intraperitoneal-dog LD50; 546 mg/kg unreported-man LDLo; mutagenic data (RTECS); reproductive effects data (RTECS); tumorigenic data (RTECS).
CARCINOGEN STATUS: Anticipated Human Carcinogen (NTP); Human Inadequate Evidence, Animal Sufficient Evidence (IARC Group-2B). Chloroform produced

benign and malignant tumors of the liver and kidney in mice following oral gavage. Administration to rats by gavage or in drinking-water increased the incidences of kidney and thyroid tumors and of neoplastic nodules of the liver.

LOCAL EFFECTS: Irritant- inhalation, skin, eye.

ACUTE TOXICITY LEVEL: Moderately toxic by ingestion; slightly toxic by inhalation and dermal absorption.

TARGET EFFECTS: Central nervous system depressant; hepatotoxin, nephrotoxin. Poisoning may also affect the heart.

AT INCREASED RISK FROM EXPOSURE: Alcoholics and persons with chronic skin, eye, liver, kidney, heart or respiratory disorders.

ADDITIONAL DATA: Use of, or exposure to, alcohol, steroids, polybrominated biphenyls, acetone, or chlordecone may enhance the toxic effects. May be excreted in breast milk. Stimulants such as epinephrine may induce ventricular fibrillation.

HEALTH EFFECTS

INHALATION:

CHLOROFORM:

IRRITANT/NARCOTIC/HEPATOTOXIN/NEPHROTOXIN.

ACUTE EXPOSURE- May cause irritation of the upper respiratory tract. Central nervous system depression may be preceded by excitation and inebriation. 1,000-2,000 ppm may cause dizziness, headache, fatigue, salivation, and nausea; 4,000 ppm may cause vomiting, serious disorientation, and a fainting feeling; 14,000-16,000 ppm may cause anesthesia and rapid loss of consciousness; more than 20,000 ppm may cause respiratory failure, cardiac arrhythmias, and death. Other symptoms may include a feeling of warmth, malaise, drowsiness, mydriasis with diminished light reflex, toxemia, loss of tendon reflexes, stupor, convulsions, coma and hypotension. Fatty changes and centrilobular necrosis of the liver and fatty degenerative changes of the kidney and heart may occur. If death does not occur immediately from respiratory arrest or ventricular fibrillation, it may occur later from liver and kidney damage.

CHRONIC EXPOSURE- Repeated exposure to 77-237 ppm has caused lassitude, dullness, urinary frequency, and gastrointestinal disturbances. Other reported symptoms include dry mouth, thirst, malaise, anorexia, headache, depression, confusion, weakness, blurred vision, paresthesias, loss of sense of balance, memory loss, tremors, anemia, kidney damage, and fatty degeneration of the liver. 17 of 68 workers exposed to 10-200 ppm for 1-4 years exhibited hepatomegaly and increased susceptibility to viral hepatitis. Exposure of rats on days 6-15 of gestation caused a high rate of resorptions, retarded fetal development, decreased fetal body measurements, and a low incidence of acaudate fetuse with imperforate anus. Mice exposed on days 8-15 of gestation had offspring with a significant increase of cleft palate. One noncorroborate study reports abnormal spermatozoa in mice exposed to levels above the TLV.

SKIN CONTACT:

CHLOROFORM:

IRRITANT.

ACUTE EXPOSURE- May cause irritation with inflammation, destruction of the epithelium, and prurulent blebs. Application to rabbit skin for 24

hours caused hyperemia and moderate necrosis. Some absorption occurred resulting in weight loss and degenerative kidney changes, however doses as high as 3980 mg/kg were survived.

CHRONIC EXPOSURE- Repeated or prolonged exposure may cause dermatitis with drying, cracking, and redness. If sufficient amounts are absorbed, systemic effects may occur.

EYE CONTACT:
CHLOROFORM:
IRRITANT.

ACUTE EXPOSURE- High vapor concentrations may cause stinging, irritation, and blepharospasm. Contact with the liquid may also cause burning pain, lacrimation, and redness. The corneal epithelium may be injured and partially lost, however, the eyes return to normal in 1-3 days. Long exposure of the cornea during general anesthesia has caused persistent injury.

CHRONIC EXPOSURE- Repeated or prolonged contact with irritants may cause conjunctivitis.

INGESTION:
CHLOROFORM:
NARCOTIC/HEPATOTOXIN/NEPHROTOXIN/CARCINOGEN.

ACUTE EXPOSURE- May cause burning of the mouth, throat, esophagus, and stomach, nausea, vomiting, diarrhea, abdominal and substernal pain, cold, clammy skin, cyanosis of the extremities and face, muscle cramps, mydriasis, hypotension, peripheral vasodilation, irregular respiration, respiratory failure, unconsciousness, and liver damage. The mean lethal dose in humans is about 1 ounce. Aspiration may occur and result in chemical pneumonitis. 250 mg/kg caused depression, profound sleep, dyspnea, anorexia, hematuria, and liver and kidney changes in rats.

CHRONIC EXPOSURE- Repeated ingestion may cause liver and kidney damage. In feeding studies, there was an increased incidence of benign and malignant tumors of the liver and kidneys in mice and of tumors of the kidney and thyroid and neoplastic nodules in the liver in rats. Reproductive effects have been reported in animals.

SECTION 12 ECOLOGICAL INFORMATION

ENVIRONMENTAL IMPACT RATING (0-4): no data available

ACUTE AQUATIC TOXICITY: no data available

DEGRADABILITY: no data available

LOG BIOCONCENTRATION FACTOR (BCF): no data available

LOG OCTANOL/WATER PARTITION COEFFICIENT: no data available

SECTION 13 DISPOSAL INFORMATION

Observe all federal, state and local regulations when disposing of this substance.

Disposal must be in accordance with standards applicable to generators of hazardous waste, 40CFR 262. EPA hazardous waste number uo44.

Chloroform - Regulatory level: 6.0 mg/l (TCLP-40 CFR 261 Appendix II) materials which contain the above substance at or above the TCLP regulatory level meet the EPA toxicity characteristic, and must be disposed of in accordance with 40 CFR part 262. EPA Hazardous Waste Number D022.

US EPA RCRA Hazardous Waste Number: RCRA U044

SECTION 14 TRANSPORTATION INFORMATION

DEPARTMENT OF TRANSPORTATION HAZARD CLASSIFICATION 49-CFR 172.101:
ORM-A

Department of Transportation labeling requirements 49-CFR 172.101 and SUBPART E:
None

DEPARTMENT OF TRANSPORTATION PACKAGING REQUIREMENTS: 49-CFR 173.630
EXCEPTIONS: 49-CFR 173.505

Final rule on hazardous materials regulations (HMR, 49 CFR parts 171-180), docket numbers HM-181, HM-181a, HM-181b, HM-181c, HM-181d and HM-204. Effective date October 1, 1991. However, compliance with the regulations is authorized on and after January 1, 1991. (55 FR 52402, 12/21/90)

Except for explosives, inhalation hazards, and infectious substances, the effective date for hazard communication requirements is extended to October 1, 1993. (56 FR 47158, 09/18/91)

U.S. DEPARTMENT OF TRANSPORTATION SHIPPING NAME-ID NUMBER, 49 CFR 172.101:
Chloroform-UN 1888

U.S. DEPARTMENT OF TRANSPORTATION HAZARD CLASS OR DIVISION, 49 CFR 172.101:
6.1 - Poisonous materials

U.S. DEPARTMENT OF TRANSPORTATION PACKING GROUP, 49 CFR 172.101:
PG II

U.S. DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS, 49 CFR 172.101 AND SUBPART E:
Poison

U.S. DEPARTMENT OF TRANSPORTATION PACKAGING AUTHORIZATIONS:
EXCEPTIONS: None
NON-BULK PACKAGING: 49 CFR 173.202
BULK PACKAGING: 49 CFR 173.241

U.S. DEPARTMENT OF TRANSPORTATION QUANTITY LIMITATIONS 49 CFR 172.101:
PASSENGER AIRCRAFT OR RAILCAR: 5 l
CARGO AIRCRAFT ONLY: 60 l

SECTION 15 REGULATORY INFORMATION

TSCA STATUS: Y

CERCLA SECTION 103 (40CFR302.4):	Y	10	pounds RQ
SARA SECTION 302 (40CFR355.30):	Y	10,000	pounds TPQ
SARA SECTION 304 (40CFR355.40):	Y	5000	pounds RQ
SARA SECTION 313 (40CFR372.65):	Y		
OSHA PROCESS SAFETY (29CFR1910.119):	N		
CALIFORNIA PROPOSITION 65:	Y		

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40 CFR 370.21)

ACUTE HAZARD:	Y
CHRONIC HAZARD:	Y
FIRE HAZARD:	N
REACTIVITY HAZARD:	N
SUDDEN RELEASE HAZARD:	N

SECTION 16 OTHER

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COMPOUND NAME 1,1,2,2-TETRACHLOROETHANE

CAS #	79-34-5		
USEPA HAZ WASTE CODE	U209		
IDLH	150 PPM		
TLV-TWA	1 PPM	TLV-STEL	TLV-C
VAPOR PRESSURE (mmHg) @ 20 °C	6 @ 25 °C		
NFPA-H[1]	2	NFPA-F[2]	0
NFPA-R[3]	0	NFPA-S[4]	-
US DOT CLASSIFICATION	6.1- POISON		
HAZARDOUS DECOMPOSITION PRODUCTS	CARBON MONOXIDE, OXIDES OF CHLORINE		
OTHER	CONTACT WITH WATER WILL DEGRADE AND DECOMPOSE THIS LIQUID		

[1] NFPA HEALTH [2] NFPA FIRE [3] NFPA REACTIVITY [4] NFPA SPECIFIC HAZARD U=UNKNOWN

Material Safety Data Sheet

Genium Publishing Corporation
1145 Catalyn Street, Schenectady, NY 12303
(518) 377-8854
[illegible], to be used as reference

Product: 1,1,2,2-TETRACHLOROETHANE

MSDS No: [illegible]
Date: November, 1988

National Paint and Coatings Association	HEALTH HAZARD : [illegible] - Moderate
	FLAMMABILITY HAZARD : 0 - Minimal
Hazardous Material Identification System	REACTIVITY HAZARD : 0 - Minimal
	PERSONAL PROTECTION : SEE SECT. 8

SECTION I. MATERIAL IDENTIFICATION

Trade/Material Name: 1,1,2,2-TETRACHLOROETHANE

Description: Used as a solvent primarily for cleaning and extraction procedures and as a chemical intermediate in the manufacture of trichloroethylene and tetrachloroethylene; and as an analytic reagent by textile manufacturers in polymer characterization tests.

Other Designations: Acetylene Tetrachloride; sym-Tetrachloroethane; $CHCl_2CHCl_2$

CAS: 0079-34-5

R 1
I 4
S -
K -

Manufacturer: Contact your supplier or distributor. Consult the latest edition of the Chemicalweek Buyers' Guide (Genium ref. 73) for a list of suppliers.

SECTION II. INGREDIENTS AND HAZARDS

Ingredient Name:	CAS Number:	Percent:	Exposure Limits:
1,1,2,2-Tetrachloroethane	0079-34-5	Ca 100	OSHA PEL (Skin*) 8-Hr TWA: 1 ppm, 7 mg/m^3 ACGIH TLV (Skin*), 1988-89 TLV-TWA: 1 ppm, 7 mg/m^3 Toxicity Data** Human, Oral, TD_{Lo}: 30 mg/kg Human, Inhalation, TC_{Lo}: 1000 mg/m^3 (30 Mins) Rat, Oral, LD_{50}: 800 mg/kg

* This material can be absorbed through intact skin, which contributes to overall exposure.
** See NIOSH, RTECS (KI8575000), for additional data with references to reproductive, tumorigenic, and irritative effects.

 MSDS 677 continues on page 2

[illegible]
[illegible] Schenectady, NY [illegible]
(518) 377-8854
[illegible]

Product: [illegible]-TETRACHLOROETHANE

MSDS No: Genium [illegible]
Date: November [illegible]

SECTION III PHYSICAL DATA

Appearance & Odor: [illegible] colorless, nonflammable, heavy, mobile liquid; sweetish, suffocating, characteristic chloroform odor. The odor recognition threshold is reported to be less than 3 ppm.

Boiling point: [illegible] (146 [illegible])
Vapor pressure: [illegible] Torr [illegible] 77 [illegible] (25 [illegible]) *
Water solubility (%): Insoluble

Specific gravity (H_2O=1): 1.58658 at 77 [illegible] (25 [illegible])
Melting point: -47 [illegible] (-44 [illegible])
% volatile by volume: Ca 100
Molecular weight: 168 Grams/Mole

* At 77 [illegible] (25 [illegible]) the concentration of 1,1,2,2-tetrachloroethane in saturated air is approximately 7900 ppm.

SECTION IV. FIRE AND EXPLOSION DATA

Flash Point (method): *
Limits: LEL %: *
UEL %: *

NFPA Fire Hazard Symbol Codes: Flammability: 0 **Health:** [illegible] **Reactivity:** 0 **Special:** -**

Extinguishing Media: [illegible]-Tetrachloroethane does not burn. Use extinguishing agents that will put out the surrounding fire.

Autoignition Temp: *

Unusual fire or explosion hazards: None reported.

Special fire-fighting procedures: Wear a self-contained breathing apparatus (SCBA) with a full facepiece operated in the pressure-demand or positive-pressure mode to protect against the effects of the nearby fire.

** Values determined by Genium. Not found in NFPA Guidebook.

Genium Publishing Corporation
1145 Catalyn Street, Schenectady, NY 12303
(518) 377-8854
From Genium Publication, to be used as reference

Product: 1,1,2,2-TETRACHLOROETHANE

MSDS No: Genium [illegible]
Date: November, 1988

SECTION V. REACTIVITY DATA

Material is stable in closed containers during routine operations at room temperature. Hazardous polymerization cannot occur.

Chemical incompatibilities: Hazardous reactions between 1,1,2,2-tetrachloroethane and 2,4-dinitrophenyl disulfide, nitrogen tetroxide, chemically active metals such as potassium; and strong caustics such as potassium hydroxide, sodium, sodium-potassium alloy, hot iron, aluminum, and zinc in the presence of steam are reported.

Conditions to avoid: Prevent exposure to the incompatible chemicals listed above. Contact with water causes appreciable hydrolysis that will degrade and decompose this liquid.

Hazardous decomposition Products: Thermal-oxidative degradation of 1,1,2,2-tetrachloroethane can produce highly toxic gases such as carbon monoxide (CO) and oxides of chlorine (ClO_x).

SECTION VI. HEALTH HAZARD INFORMATION

This product is considered a carcinogen by NIOSH.

Summary of risks: 1,1,2,2-Tetrachloroethane is absorbed through intact skin in significant amounts; one human fatality has been attributed to this route of exposure. This liquid is considered to be one of the most toxic of the common chlorinated hydrocarbons, particularly with respect to the liver. Severely acute exposure causes depression of the central nervous system (CNS), which can cause death within 12 hours.

Medical conditions which may be aggravated by contact: None reported.

Target organs: Skin, eyes, respiratory system, CNS, gastrointestinal system, liver, and kidneys.

Primary entry route(s): Inhalation, skin contact/absorption.

Acute effects: The initial symptoms of exposure are lacrimation, salivation, and irritation of the nose and throat; continued exposure can lead to nausea, vomiting, and narcosis. Also, low blood pressure and cardiac rhythm abnormalities; respiratory depression; nausea; vomiting; burns of the esophagus, and diarrhea; and anesthesia with dizziness leading to loss of consciousness and coma; plus possible transient liver and kidney changes.

Genium Publishing Corporation
[illegible] Catalyn Street, Schenectady, NY [illegible]
(518) 377-8854
From Genium's collection, to be used as reference

Product: [illegible] TETRACHLOROETHANE

MSDS No: Genium / [illegible]77
Date: [illegible] 1988

HEALTH HAZARD INFORMATION continued from page [illegible]

Chronic effect(s): The two sets of manifestations are (1) malaise, drowsiness, decreased appetite, then nausea and catching, a bad taste in the throat, constipation, headache, pale stools, jaundice, and dark urine, as well as mental confusion, stupor, and coma; and (2) hand tremors, sensation of deafness, numbness in hands and feet, a decrease in reflexes, headache, and nausea.

First aid:

Eye contact: Immediately flush eyes, including under the eyelids, gently but thoroughly with flooding amounts of running water for at least 15 minutes.

Skin contact: Rinse the affected areas with flooding amounts of water, then wash it with soap and water.

Inhalation: Remove the exposed person to fresh air; restore and/or support his or her breathing as needed. Have qualified medical personnel administer oxygen as required. Keep the exposed person warm and at rest until medical help is available.

Ingestion: Unlikely. Should this type of exposure occur, give the exposed person 2 glasses of water to drink and induce vomiting, then repeat this procedure.

Get medical help (in plant, paramedic, community) for all exposures. Seek prompt medical assistance for further treatment, observation, and support after first aid. Note to Physician: Workers exposed to this liquid should be evaluated with a full battery of tests for the liver, kidneys, and CNS, as well as the blood.

SECTION VII. SPILL, LEAK AND DISPOSAL PROCEDURES

Spill / Leak procedures: Notify safety personnel, evacuate unnecessary personnel, and provide adequate ventilation. Cleanup personnel must be properly clothed and equipped to protect the skin and eyes against any contact with the liquid as well as inhalation of its vapor (see sect.8). Vacuum the spilled 1,1,2,2-tetrachloroethane and pump it into suitable containers for disposal.

Waste management / Disposal: Contact your supplier or a licensed contractor for detailed recommendations. Follow Federal, state, and local regulations.

[illegible] Publishing Corporation
[illegible] Schenectady, [illegible]
[illegible] 377-8854
[illegible]

Product: [illegible]
[illegible]

MSDS No: [illegible]
Date: [illegible]

SPILL, LEAK AND DISPOSAL PROCEDURES continued from page 4

OSHA Designations
Listed as an Air Contaminant (29 CFR 1910.1000 Subpart Z).

RCRA Designations (40 CFR 302.4)
RCRA Hazardous Waste, No. U209
RCRA Hazardous Substance, Reportable Quantity: 1 lb (0.454 kg), per the Clean Water Act (CWA), Section 307 (a); and the Resource Conservation and Recovery Act (RCRA), Section 3001.

SECTION VIII. SPECIAL PROTECTION INFORMATION

Personal protective equipment:

Goggles: Always wear protective eyeglasses or chemical safety goggles. Where splashing of this liquid is possible, wear a full face shield. Follow OSHA eye- and face-protection regulations (29 CFR 1910.133).

Respirator: Use a NIOSH-approved respirator per Genium reference 88 for the maximum-use concentrations and/or the exposure limits cited in section [illegible]. Follow OSHA respirator regulations (29 CFR [illegible]). For emergency or nonroutine operations (spills or cleaning reactor vessels and storage tanks), wear an SCBA. Warning: Air-purifying respirators will not protect workers in oxygen-deficient atmospheres.

Other: Wear impervious gloves, boots, aprons, and gauntlets to prevent skin contact with this liquid.

Workplace considerations:

Ventilation: Install and operate general and local ventilation systems powerful enough to maintain airborne levels of this material below the OSHA PEL standard cited in section 2. Local exhaust ventilation is preferred because it prevents dispersion of the contaminant into the general work area by eliminating it at its source. Consult the latest edition of Genium reference 103 for detailed recommendations.

[illegible] Corporation
[illegible] Schenectady, NY [illegible]
[illegible] 377-8854
from Benium[illegible] [illegible] reference

Product: [illegible] TETRACHLOROETHANE

MSDS No: [illegible]nium [illegible]
Date: [illegible] [illegible]88

SPECIAL PROTECTION INFORMATION continued from page 5

Safety stations:
Make emergency eyewash stations, safety/quick-drench showers, and [illegible] facilities available in work areas.

Contaminated equipment:
[illegible] lenses pose a special hazard; soft lenses may absorb irritants, and all lenses concentrate them. Do not wear contact lenses in any work area. Remove contaminated clothing and launder it before wearing it again; clean this material from your shoes and equipment.

Practice good personal hygiene; always wash thoroughly after using this material and before eating, drinking, smoking, using the toilet, or applying cosmetics. Keep it off your clothing and equipment. Avoid transferring it from your hands to your mouth while eating, drinking, or smoking. Do not eat, drink, or smoke in any work area. Do not inhale 1,1,2,2-tetrachloroethane vapor.

SECTION IX. SPECIAL PRECAUTIONS

Storage segregation: Store 1,1,2,2-tetrachloroethane in closed, airtight containers in a cool, dry, well-ventilated area away from incompatible chemicals (see sect. 5).

Special handling / storage: Provide storage areas with adequate ventilation to prevent concentrations of the vapor from building up beyond the occupational exposure limits cited in section 2.

Transportation Data (49 CFR 172.101-2)

DOT Shipping Name: Tetrachloroethane
DOT Packaging Requirements: 49 CFR 173.620
DOT Packaging Exceptions: 49 CFR 173.505

IMO Shipping Name: 1,1,2,2-Tetrachloroethane
IMO Hazard Class: 6.1
IMO Label: Poison
IMDG Packaging Group: II

DOT Class: ORM-A **UN Register:** UN1702
Data source code(s): 1, 38, 84-94, 100, 116, 117, 120, 122.

Genium Publishing [illegible]
[illegible] Schenectady, NY [illegible]
[illegible]

Product: [illegible]
[illegible]TETRACHLOROETHANE

MSDS No: [illegible]
Date: [illegible]

SPECIAL PRECAUTIONS continued from page [illegible]

Prepared/revised by: [illegible]

November, 1988

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COMPOUND NAME 1,1,2-TRICHLOROETHANE

CAS #	79-00-5		
USEPA HAZ WASTE CODE	U227		
IDLH	50 PPM		
TLV-TWA	10 PPM	TLV-STEL	TLV-C
VAPOR PRESSURE (mmHg) @ 20 °C	17		
NFPA-H [1]	3	NFPA-F [2]	1
NFPA-R [3]	0	NFPA-S [4]	-
US DOT CLASSIFICATION	NOT LISTED		
HAZARDOUS DECOMPOSITION PRODUCTS	HIGHLY TOXIC FUMES OF PHOSGENE, TOXIC AND CORROSIVE FUMES OF CHLORIDES AND OXIDES OF CARBON		
OTHER			

[1] NFPA HEALTH [2] NFPA FIRE [3] NFPA REACTIVITY [4] NFPA SPECIFIC HAZARD U=UNKNOWN

OHS26380

SECTION 1 CHEMICAL PRODUCTS & COMPANY IDENTIFICATION

OCCUPATIONAL HEALTH SERVICES, INC.
11 WEST 42ND STREET, 12TH FLOOR
NEW YORK, NEW YORK 10036
1-800-445-MSDS (1-800-445-6737) OR
1-212-789-3535

FOR EMERGENCY SOURCE INFORMATION
CONTACT: 1-615-366-2000

CAS NUMBER: 79-00-5
RTECS NUMBER: KJ3150000

SUBSTANCE: 1,1,2-TRICHLOROETHANE

TRADE NAMES/SYNONYMS:
VINYL TRICHLORIDE; BETA-TRICHLOROETHANE; ETHANE, 1,1,2-TRICHLORO-; ETHANE TRICHLORIDE; 1,2,2-TRICHLOROETHANE; 1,1,2-TRICHLORETHANE; 1,1,2-TCE; RCRA U227; C2H3CL3; OHS26380

CHEMICAL FAMILY:
HALOGEN COMPOUND, ALIPHATIC

SECTION 2 COMPOSITION/INFORMATION ON INGREDIENTS

COMPONENT: 1,1,2-TRICHLOROETHANE
CAS NUMBER: 79-00-5
PERCENTAGE: 100.0
OTHER CONTAMINANTS: NONE

SECTION 3 HAZARDS IDENTIFICATION

CERCLA RATINGS (SCALE 0-3): HEALTH=3 FIRE=1 REACTIVITY=0 PERSISTENCE=3
NFPA RATINGS (SCALE 0-4): HEALTH=3 FIRE=1 REACTIVITY=0

EMERGENCY OVERVIEW:
1,1,2-TRICHLOROETHANE IS A CLEAR LIQUID WITH A MILD, SWEET ODOR. HARMFUL IF INHALED. MAY CAUSE LIVER DAMAGE. MAY AFFECT THE CENTRAL NERVOUS SYSTEM. CAUSES RESPIRATORY TRACT, SKIN AND EYE IRRITATION. AVOID BREATHING VAPOR OR MIST. AVOID CONTACT WITH EYES, SKIN AND CLOTHING. KEEP CONTAINER TIGHTLY CLOSED. WASH THOROUGHLY AFTER HANDLING. USE ONLY WITH ADEQUATE VENTILATION.

POTENTIAL HEALTH EFFECTS:
SHORT TERM EXPOSURE: MAY CAUSE IRRITATION OF THE NOSE, THROAT, SKIN, AND EYES. ADDITIONAL EFFECTS MAY INCLUDE DRUNKENESS, VOMITING, DIGESTIVE DISORDERS, LUNG DAMAGE, WEAKNESS, NUMBNESS, HEADACHE, CONFUSION, IRREGULAR HEARTBEAT, HEART FAILURE, LIVER AND KIDNEY DAMAGE AND UNCONSCIOUSNESS. MAY ALSO CAUSE DEATH.
LONG TERM EXPOSURE: IN ADDITION TO EFFECTS FROM SHORT TERM EXPOSURE, TINGLING SENSATION, NERVOUSNESS AND PARALYSIS MAY OCCUR.

CARCINOGEN STATUS:
OSHA: N
NTP: N
IARC: N

SECTION 4 FIRST AID MEASURES

INHALATION:
FIRST AID- REMOVE FROM EXPOSURE AREA TO FRESH AIR IMMEDIATELY. IF BREATHING HAS STOPPED, GIVE ARTIFICIAL RESPIRATION. MAINTAIN AIRWAY AND BLOOD PRESSURE AND ADMINISTER OXYGEN IF AVAILABLE. KEEP AFFECTED PERSON WARM AND AT REST. TREAT SYMPTOMATICALLY AND SUPPORTIVELY. ADMINISTRATION OF OXYGEN SHOULD BE PERFORMED BY QUALIFIED PERSONNEL. GET MEDICAL ATTENTION IMMEDIATELY.

SKIN CONTACT:
FIRST AID- REMOVE CONTAMINATED CLOTHING AND SHOES IMMEDIATELY. WASH AFFECTED AREA WITH SOAP OR MILD DETERGENT AND LARGE AMOUNTS OF WATER UNTIL NO EVIDENCE OF CHEMICAL REMAINS (APPROXIMATELY 15-20 MINUTES). GET MEDICAL ATTENTION IMMEDIATELY.

EYE CONTACT:
FIRST AID- WASH EYES IMMEDIATELY WITH LARGE AMOUNTS OF WATER OR NORMAL SALINE, OCCASIONALLY LIFTING UPPER AND LOWER LIDS, UNTIL NO EVIDENCE OF CHEMICAL REMAINS (APPROXIMATELY 15-20 MINUTES). GET MEDICAL ATTENTION IMMEDIATELY.

INGESTION:
FIRST AID- REMOVE BY GASTRIC LAVAGE OR EMESIS. MAINTAIN BLOOD PRESSURE AND AIRWAY. GIVE OXYGEN IF RESPIRATION IS DEPRESSED. DO NOT PERFORM GASTRIC LAVAGE OR EMESIS IF VICTIM IS UNCONSCIOUS. GET MEDICAL ATTENTION IMMEDIATELY (DREISBACH, HANDBOOK OF POISONING, 12TH ED.). ADMINISTRATION OF GASTRIC LAVAGE OR OXYGEN SHOULD BE PERFORMED BY QUALIFIED MEDICAL PERSONNEL.

NOTE TO PHYSICIAN
ANTIDOTE:
NO SPECIFIC ANTIDOTE. TREAT SYMPTOMATICALLY AND SUPPORTIVELY.

SECTION 5 FIRE FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:
SLIGHT FIRE HAZARD WHEN EXPOSED TO HEAT OR FLAME.

EXTINGUISHING MEDIA:
DRY CHEMICAL OR CARBON DIOXIDE
(1990 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.5).

FOR LARGER FIRES, USE WATER SPRAY, FOG OR REGULAR FOAM
(1990 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.5).

FIREFIGHTING:

APPLY COOLING WATER TO SIDES OF CONTAINERS THAT ARE EXPOSED TO FLAMES UNTIL WELL AFTER FIRE IS OUT. STAY AWAY FROM ENDS OF TANKS. ISOLATE FOR 1/2 MILE IN ALL DIRECTIONS IF TANK, RAIL CAR OR TANK TRUCK IS INVOLVED IN FIRE (1990 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.5, GUIDE PAGE 74).

EXTINGUISH USING AGENTS FOR SURROUNDING FIRE. COOL FIRE-EXPOSED CONTAINERS WITH FLOODING AMOUNTS OF WATER APPLIED FROM AS FAR A DISTANCE AS POSSIBLE. DO NOT ALLOW RUN-OFF WATER INTO SEWERS AND WATER SOURCES. AVOID BREATHING VAPORS.

LOWER FLAMMABLE LIMIT: 6.0%
UPPER FLAMMABLE LIMIT: 15.5%
AUTOIGNITION: 860 F (460 C)

HAZARDOUS COMBUSTION PRODUCTS:
THERMAL DECOMPOSITION PRODUCTS MAY INCLUDE HIGHLY TOXIC FUMES OF PHOSGENE, TOXIC AND CORROSIVE FUMES OF CHLORIDES, AND OXIDES OF CARBON.

SECTION 6 ACCIDENTAL RELEASE MEASURES

OCCUPATIONAL SPILL:
SHUT OFF IGNITION SOURCES. STOP LEAK IF YOU CAN DO IT WITHOUT RISK. FOR SMALL LIQUID SPILLS, TAKE UP WITH SAND, EARTH OR OTHER ABSORBENT MATERIAL. FOR LARGER SPILLS, DIKE FAR AHEAD OF SPILL FOR LATER DISPOSAL. NO SMOKING, FLAMES OR FLARES IN HAZARD AREA! KEEP UNNECESSARY PEOPLE AWAY.

REPORTABLE QUANTITY (RQ): 100 POUNDS
THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT (SARA) SECTION 304 REQUIRES THAT A RELEASE EQUAL TO OR GREATER THAN THE REPORTABLE QUANTITY FOR THIS SUBSTANCE BE IMMEDIATELY REPORTED TO THE LOCAL EMERGENCY PLANNING COMMITTEE AND THE STATE EMERGENCY RESPONSE COMMISSION (40 CFR 355.40). IF THE RELEASE OF THIS SUBSTANCE IS REPORTABLE UNDER CERCLA SECTION 103, THE NATIONAL RESPONSE CENTER MUST BE NOTIFIED IMMEDIATELY AT (800) 424-8802 OR (202) 426-2675 IN THE METROPOLITAN WASHINGTON, D.C. AREA (40 CFR 302.6).

WATER SPILL:
THE CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 (PROPOSITION 65) PROHIBITS CONTAMINATING ANY KNOWN SOURCE OF DRINKING WATER WITH SUBSTANCES KNOWN TO CAUSE CANCER AND/OR REPRODUCTIVE TOXICITY.

SECTION 7 HANDLING AND STORAGE

STORAGE:
OBSERVE ALL FEDERAL, STATE AND LOCAL REGULATIONS WHEN STORING OR DISPOSING OF THIS SUBSTANCE. FOR ASSISTANCE, CONTACT THE DISTRICT DIRECTOR OF THE ENVIRONMENTAL PROTECTION AGENCY.

PROTECT AGAINST PHYSICAL DAMAGE. STORE IN A COOL, DRY, WELL VENTILATED LOCATION AWAY FROM ANY AREA WHERE THE FIRE HAZARD MAY BE ACUTE. OUTSIDE OR

DETACHED STORAGE IS PREFERRED (NFPA 49, HAZARDOUS CHEMICALS DATA, 1975).

STORE AWAY FROM INCOMPATIBLE SUBSTANCES.

SECTION 8 EXPOSURE CONTROLS/PERSONAL PROTECTION

EXPOSURE LIMITS:
1,1,2-TRICHLOROETHANE
10 PPM (55 MG/M3) OSHA TWA (SKIN)
10 PPM (55 MG/M3) ACGIH TWA (SKIN)
10 PPM (55 MG/M3) NIOSH RECOMMENDED TWA (SKIN)
10 PPM (55 MG/M3) DFG MAK TWA (SKIN);
50 PPM (275 MG/M3) DFG MAK 30 MINUTE PEAK, AVERAGE VALUE, 2 TIMES/SHIFT

MEASUREMENT METHOD: CHARCOAL TUBE; CARBON DISULFIDE; GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION; (NIOSH VOL. III # 1003, HALOGENATED HYDROCARBONS).

100 POUNDS CERCLA SECTION 103 REPORTABLE QUANTITY
SUBJECT TO SARA SECTION 313 ANNUAL TOXIC CHEMICAL RELEASE REPORTING
SUBJECT TO CALIFORNIA PROPOSITION 65 CANCER AND/OR REPRODUCTIVE TOXICITY WARNING AND RELEASE REQUIREMENTS-(OCTOBER 1,1990)

VENTILATION:
PROVIDE LOCAL EXHAUST OR PROCESS ENCLOSURE VENTILATION TO MEET PUBLISHED EXPOSURE LIMITS.

EYE PROTECTION:
EMPLOYEE MUST WEAR SPLASH-PROOF OR DUST-RESISTANT SAFETY GOGGLES TO PREVENT EYE CONTACT WITH THIS SUBSTANCE.

EMERGENCY EYE WASH: WHERE THERE IS ANY POSSIBILITY THAT AN EMPLOYEE'S EYES MAY BE EXPOSED TO THIS SUBSTANCE, THE EMPLOYER SHOULD PROVIDE AN EYE WASH FOUNTAIN WITHIN THE IMMEDIATE WORK AREA FOR EMERGENCY USE.

CLOTHING:
EMPLOYEE MUST WEAR APPROPRIATE PROTECTIVE (IMPERVIOUS) CLOTHING AND EQUIPMENT TO PREVENT REPEATED OR PROLONGED SKIN CONTACT WITH THIS SUBSTANCE.

GLOVES:
EMPLOYEE MUST WEAR APPROPRIATE PROTECTIVE GLOVES TO PREVENT CONTACT WITH THIS SUBSTANCE.

RESPIRATOR:
THE FOLLOWING RESPIRATORS AND MAXIMUM USE CONCENTRATIONS ARE RECOMMENDATIONS BY THE U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, NIOSH POCKET GUIDE TO CHEMICAL HAZARDS; NIOSH CRITERIA DOCUMENTS OR BY THE U.S. DEPARTMENT OF LABOR, 29 CFR 1910 SUBPART Z.
THE SPECIFIC RESPIRATOR SELECTED MUST BE BASED ON CONTAMINATION LEVELS FOUND IN THE WORK PLACE, MUST NOT EXCEED THE WORKING LIMITS OF THE RESPIRATOR AND BE JOINTLY APPROVED BY THE NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH AND THE MINE SAFETY AND HEALTH ADMINISTRATION (NIOSH-MSHA).

1,1,2-TRICHLOROETHANE:
AT ANY DETECTABLE CONCENTRATION:
ANY SELF-CONTAINED BREATHING APPARATUS WITH A FULL FACEPIECE AND OPERATED IN A PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE.
ANY SUPPLIED-AIR RESPIRATOR WITH A FULL FACEPIECE AND OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE IN COMBINATION WITH AN AUXILIARY SELF-CONTAINED BREATHING APPARATUS OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE.

ESCAPE- ANY AIR-PURIFYING FULL FACEPIECE RESPIRATOR (GAS MASK) WITH A CHIN-STYLE OR FRONT- BACK-MOUNTED ORGANIC VAPOR CANISTER.
ANY APPROPRIATE ESCAPE-TYPE SELF-CONTAINED BREATHING APPARATUS.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

ANY SELF-CONTAINED BREATHING APPARATUS THAT HAS A FULL FACEPIECE AND IS OPERATED IN A PRESSURE-DEMAND OR OTHER POSITIVE-PRESSURE MODE.

ANY SUPPLIED-AIR RESPIRATOR THAT HAS A FULL FACEPIECE AND IS OPERATED IN A PRESSURE-DEMAND OR OTHER POSITIVE-PRESSURE MODE IN COMBINATION WITH AN AUXILIARY SELF-CONTAINED BREATHING APPARATUS OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE-PRESSURE MODE.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

DESCRIPTION: CLEAR, COLORLESS LIQUID WITH A MILD CHLOROFORM-LIKE ODOR.
MOLECULAR WEIGHT: 133.40
MOLECULAR FORMULA: C-H2-CL-C-H-CL2
BOILING POINT: 235-237 F (113-114 C)
MELTING POINT: -35 F (-37 C)
VAPOR PRESSURE (MMHG): 17 MMHG @ 20 C
VAPOR DENSITY (AIR=1): 4.63
SPECIFIC GRAVITY (WATER=1) : 1.4416
WATER SOLUBILITY: 0.45% @ 20 C
% VOLATILES: 100%
SOLVENT SOLUBILITY: SOLUBLE IN CHLOROFORM, ESTERS, KETONES, ALCOHOL, ETHER.

SECTION 10 STABILITY AND REACTIVITY

REACTIVITY:
STABLE UNDER NORMAL TEMPERATURES AND PRESSURES.

CONDITIONS TO AVOID:
MAY BURN BUT DOES NOT IGNITE READILY. CONTAINER MAY EXPLODE IN HEAT OF FIRE.

INCOMPATIBILITIES:
1,1,2-TRICHLOROETHANE:
ACIDS (STRONG): EVOLVES TOXIC AND CORROSIVE HYDROGEN CHLORIDE GAS.
ALKALI METALS: POSSIBLE VIOLENT REACTION.
ALUMINUM: INCOMPATIBLE.
BARIUM: POSSIBLE VIOLENT REACTION.

CAUSTICS (STRONG): INCOMPATIBLE.
LITHIUM: POSSIBLE VIOLENT REACTION.
MAGNESIUM: POSSIBLE VIOLENT REACTION.
OXIDIZERS (STRONG): FIRE AND EXPLOSION HAZARD.
PLASTICS, RUBBER, COATINGS: MAY BE ATTACKED.
POTASSIUM AND ALLOYS: FORMS SHOCK-SENSITIVE MIXTURE.
SODIUM AND ALLOYS: FORMS SHOCK-SENSITIVE MIXTURE.
TITANIUM: POSSIBLE VIOLENT REACTION.

HAZARDOUS DECOMPOSITION:
THERMAL DECOMPOSITION PRODUCTS MAY INCLUDE HIGHLY TOXIC FUMES OF PHOSGENE, TOXIC AND CORROSIVE FUMES OF CHLORIDES, AND OXIDES OF CARBON.

POLYMERIZATION:
HAZARDOUS POLYMERIZATION HAS NOT BEEN REPORTED TO OCCUR UNDER NORMAL TEMPERATURES AND PRESSURES.

SECTION 11 TOXICOLOGY INFORMATION

1,1,2-TRICHLOROETHANE:
IRRITATION DATA: 500 MG OPEN SKIN-RABBIT MILD; 810 MG/24 HOURS SKIN-RABBIT SEVERE; 500 MG/24 HOURS SKIN-RABBIT MILD; 1440 MG/15 MINUTES SKIN-GUINEA PIG; 162 MG EYE-RABBIT MILD; 500 MG/24 HOURS EYE-RABBIT MILD.
TOXICITY DATA: 1654 PPM/6 HOURS INHALATION-RAT LC50 (EPA, TOXICOLOGICAL PROFILE); 2000 PPM/4 HOURS INHALATION-RAT LCLO; 13100 MG/M3/4.5 HOURS INHALATION-CAT LCLO; 5377 MG/KG SKIN-RABBIT LD50; 970 MG/KG SKIN-GUINEA PIG-LDLO; 836 MG/KG ORAL-RAT LD50; 378 MG/KG ORAL-MOUSE LD50; 500 MG/KG ORAL-DOG LDLO; 500 MG/KG SUBCUTANEOUS-RABBIT LDLO; 227 MG/KG SUBCUTANEOUS-MOUSE LD50; 95 MG/KG INTRAVENOUS-DOG LDLO; 970 MG/KG INTRAPERITONEAL-GUINEA PIG LDLO; 450 MG/KG INTRAPERITONEAL-DOG LD50; 494 MG/KG INTRAPERITONEAL-MOUSE LD50; 265 MG/KG INTRAPERITONEAL-RAT LD50; MUTAGENIC DATA (RTECS); REPRODUCTIVE EFFECTS DATA (RTECS); TUMORIGENIC DATA (RTECS).
CARCINOGEN STATUS: ANIMAL LIMITED EVIDENCE (IARC GROUP-3). TWO-YEAR STUDIES WERE DONE BY ORAL ADMINISTRATION USING MALE AND FEMALE MICE AND RATS AND BY SUBCUTANEOUS INJECTION IN RATS. ORAL ADMINISTRATION PRODUCED HEPATOCELLULAR NEOPLASMS AND ADRENAL PHAEOCHROMOCYTOMAS IN BOTH SEXES OF MICE BUT DID NOT SIGNIFICANTLY INCREASE THE PROPORTION OF RATS WITH NEOPLASMS AT ANY SITE COMPARED TO UNTREATED CONTROLS. SUBCUTANEOUS INJECTION TO RATS DID NOT INCREASE THE OCCURANCE OF NEOPLASMS.
LOCAL EFFECTS: IRRITANT- INHALATION, SKIN, EYES.
ACUTE TOXICITY LEVEL: MODERATELY TOXIC BY INHALATION AND INGESTION; SLIGHTLY TOXIC BY DERMAL ABSORPTION.
TARGET EFFECTS: CENTRAL NERVOUS SYSTEM DEPRESSANT; HEPATOTOXIN.
AT INCREASED RISK FROM EXPOSURE: PERSONS WITH A HISTORY OF CHRONIC RESPIRATORY, LIVER OR KIDNEY DISEASE OR DIABETES.
ADDITIONAL DATA: ALCOHOL MAY POTENTIATE BOTH CARDIAC, RENAL, AND HEPATIC TOXICITY. POLYBROMINATED BIPHENYLS AND ACETONE MAY INCREASE THE RENAL TOXICITY. EPINEPHRINE OR OTHER STIMULANTS MAY INDUCE VENTRICULAR ARRHYTHMIAS.

HEALTH EFFECTS

INHALATION
1,1,2-TRICHLOROETHANE:
IRRITANT/NARCOTIC/HEPATOTOXIN/TOXIC.
ACUTE EXPOSURE- MAY CAUSE RESPIRATORY TRACT IRRITATION, AND CENTRAL NERVOUS SYSTEM DEPRESSION WITH HEADACHE, DIZZINESS, INCOORDINATION, VERTIGO, FALL OF BLOOD PRESSURE, IRREGULAR HEARTBEAT, LIVER AND KIDNEY DAMAGE, ANESTHESIA, AND DEATH DUE TO RESPIRATORY FAILURE. EXPOSURE TO EXCESSIVE CONCENTRATIONS MAY CAUSE MYOCARDIAL SENSITIZATION TO EPINEPHRINE AND SUBSEQUENT DEATH DUE TO CARDIAC ARREST. RATS EXPOSED TO 250 PPM/4 HOURS SHOWED LIVER AND KIDNEY NECROSIS.
CHRONIC EXPOSURE- REPEATED OR PROLONGED EXPOSURE MAY CAUSE NERVOUSNESS, LOSS OF CONCENTRATION, PATELLAR REFLEX LOSS, HAND TREMOR, FINGER, VISUAL MUSCLE AND SOFT PALATE PARALYSIS, TASTE DISORDERS, PARESTHESIAS, AND ANESTHESIA. GASTRIC SYMPTOMS AND LIVER AND KIDNEY DAMAGE MAY OCCUR. REPEATED EXPOSURE TO 30 PPM CAUSED LIVER CHANGES IN FEMALE RATS AND AN INCREASED INCIDENCE OF PNEUMONITIS IN MALE RATS.

SKIN CONTACT
1,1,2-TRICHLOROETHANE:
IRRITANT/NARCOTIC/HEPATOTOXIN.
ACUTE EXPOSURE- DIRECT CONTACT MAY CAUSE IRRITATION, ERYTHEMA, SERIOUS EDEMA, AND NECROSIS. A SINGLE APPLICATION TO THE SKIN OF ANIMALS CAUSED ILLNESS, DELAYED RECOVERY AND LIVER AND KIDNEY INJURY.
CHRONIC EXPOSURE- REPEATED SKIN CONTACT MAY PRODUCE A DRY, SCALY, FISSURED DERMATITIS DUE TO THE DEFATTING PROPERTIES OF THE LIQUID. PROLONGED ABSORPTION THROUGH THE SKIN MAY CAUSE CENTRAL NERVOUS SYSTEM DEPRESSION AND LIVER AND KIDNEY DAMAGE.

EYE CONTACT
1,1,2-TRICHLOROETHANE:
IRRITANT.
ACUTE EXPOSURE- MAY CAUSE IRRITATION AND TRANSIENT INJURY.
CHRONIC EXPOSURE- REPEATED OR PROLONGED EXPOSURE MAY CAUSE CONJUNCTIVITIS.

INGESTION
1,1,2-TRICHLOROETHANE:
NARCOTIC/HEPATOTOXIN/LIMITED ANIMAL CARCINOGEN.
ACUTE EXPOSURE- MAY CAUSE NAUSEA, VOMITING, DIARRHEA, GASTROINTESTINAL DISTURBANCES AND ABDOMINAL PAIN FOLLOWED BY CENTRAL NERVOUS SYSTEM DEPRESSION WITH HEADACHE, DIZZINESS, WEAKNESS, INCOORDINATION, MENTAL CONFUSION, UNCONSCIOUSNESS, AND LIVER AND KIDNEY DAMAGE. DEATH MAY OCCUR FROM RESPIRATORY FAILURE OR CARDIAC ARREST FROM MYOCARDIAL SENSITIZATION. ORGANIC SOLVENTS OF THIS NATURE PRESENT AN ASPIRATION HAZARD WITH POSSIBLE PULMONARY EDEMA OR CHEMICAL PNEUMONITIS.
CHRONIC EXPOSURE- REPEATED OR PROLONGED EXPOSURE MAY CAUSE GASTRIC SYMPTOMS, FAT DEPOSITION IN THE KIDNEYS, AND LIVER DYSFUNCTION. PROLONGED GAVAGE ADMINISTRATION TO MICE RESULTED IN HEPATOCELLULAR CARCINOMAS AND ADRENAL PHEOCHROMOCYTOMAS.

SECTION 12 ECOLOGICAL INFORMATION

ENVIRONMENTAL IMPACT RATING (0-3): NO DATA AVAILABLE

ACUTE AQUATIC TOXICITY: NO DATA AVAILABLE

DEGRADABILITY: NO DATA AVAILABLE

LOG BIOCONCENTRATION FACTOR (BCF): NO DATA AVAILABLE

LOG OCTANOL/WATER PARTITION COEFFICIENT: NO DATA AVAILABLE

SECTION 13 DISPOSAL INFORMATION

RCRA HAZARDOUS WASTE: RCRA U227

WASTE DISPOSAL:
DISPOSAL MUST BE IN ACCORDANCE WITH STANDARDS APPLICABLE TO GENERATORS OF HAZARDOUS WASTE, 40CFR 262. EPA HAZARDOUS WASTE NUMBER U227.

SECTION 15 REGULATORY INFORMATION

TSCA STATUS: Y

OTHER REGULATORY INFORMATION AVAILABLE

CERCLA SECTION 103 (40CFR302.4):	Y	100 POUNDS RQ
SARA SECTION 302 (40CFR355.30):	N	
SARA SECTION 304 (40CFR355.40):	N	
SARA SECTION 313 (40CFR372.65):	Y	
OSHA PROCESS SAFETY (29CFR1910.119):	N	
CALIFORNIA PROPOSITION 65:	Y	

SARA HAZARD CATEGORIES, SARA SECTIONS 311/312 (40 CFR 370.21)

ACUTE HAZARD:	Y
CHRONIC HAZARD:	Y
FIRE HAZARD:	N
REACTIVITY HAZARD:	N
SUDDEN RELEASE HAZARD:	N

SECTION 16 OTHER

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CREATION DATE: 12/10/84 REVISION DATE: 12/30/92

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COMPOUND NAME HYDROGEN CYANIDE

CAS #	74-90-8		
USEPA HAZ WASTE CODE	P063		
IDLH	50 PPM		
TLV-TWA		TLV-STEL	TLV-C 10 PPM
VAPOR PRESSURE (mmHg) @ 20 °C	620		
NFPA-H [1]	4	NFPA-F [2]	4
NFPA-R [3]	2	NFPA-S [4]	-
US DOT CLASSIFICATION	6.1- POISON		
HAZARDOUS DECOMPOSITION PRODUCTS	CARBON DIOXIDE, CARBON MONOXIDE, TOXIC OXIDES OF NITROGEN		
OTHER	EXTREMELY TOXIC AND FLAMMABLE		

[1] NFPA HEALTH [2] NFPA FIRE [3] NFPA REACTIVITY [4] NFPA SPECIFIC HAZARD U=UNKNOWN

Material Safety Data Sheet

Genium Publishing Corporation
1145 Catalyn Street, Schenectady, NY 12303
(518) 377-8854
(Genium's collection, is to be used as reference)

Product: HYDROGEN CYANIDE

MSDS No: Genium # 686
Date: August, 1989

National Paint and Coatings Association Hazardous Material Identification System

HEALTH HAZARD	4 - Severe
FLAMMABILITY HAZARD	4 - Severe
REACTIVITY HAZARD	2 - Moderate
PERSONAL PROTECTION	SEE SECTION 8

SECTION I. MATERIAL IDENTIFICATION

Trade/Material Name: HYDROGEN CYANIDE

Description: Large-scale preparation by the catalytic oxidation of ammonia-methane mixtures. Used in the fumigation of ships, railroad cars, orchards, buildings, tobacco, and various foods. Can be produced in petroleum refining, electroplating, metallurgy, and photographic development.

Other Designations: Hydrocyanic acid; prussic acid; anhydrous hydrogen cyanide; HCN

CAS: 0074-90-8

R 1
F 4
S -
K 4

Manufacturer: Contact your supplier or distributor. Consult the latest Chemicalweek Buyers' Guide (Genium ref. 73) for a suppliers list.

SECTION II. INGREDIENTS AND HAZARDS

Ingredient Name:	CAS Number:	Percent:	Exposure Limits:
Hydrogen cyanide	0074-90-8	ca 100	OSHA PEL (Skin*) Ceiling: 10 ppm, 10 mg/m³ ACGIH TLV (Skin*), 1988-89 TLV-ceiling: 10 ppm, 10 mg/m³ NIOSH REL, 1976 10-min ceiling: 4.7 ppm CN, 5 mg CN/m³ Toxicity Data** Human, oral, LD_{Lo}: 570 µg/kg Human, inhalation, LC_{Lo}: 200 mg/m³/10 min Rat, inhalation, LC_{50}: 484 ppm/5 min

* This material can be absorbed through intact skin, which contributes to overall exposure.
** See NIOSH, RTECS (MW6825000), for additional data with references.

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Product: HYDROGEN CYANIDE

MSDS No: Genium / 686
Date: August, 1989

SECTION III. PHYSICAL DATA

Appearance & Odor: A colorless gas or blue-white liquid; a characteristic faint odor resembling bitter almonds for those individuals able to perceive its presence by smell.

Boiling point: 79 xF (26 xC)
Vapor pressure: 620 torr at 68 xF (20 xC)
Water solubility (%): Miscible
Vapor density (air=1): 0.941
Specific gravity (H_2O=1): 0.7
Melting point: 7.88 xF (-13.4 xC)
% volatile by volume: 100
Molecular weight: 27 g/mol

SECTION IV. FIRE AND EXPLOSION DATA

Flash Point (method): 0 xF (-17.78 xC) CC **Limits: LEL %:** 5.6 v/v **UEL %:** 40 v/v

NFPA Fire Hazard Symbol Codes: Flammability: 4 **Health:** 4 **Reactivity:** 2 **Special:** --

Extinguishing Media: Hydrogen cyanide is an extremely toxic, flammable material. In advanced or massive fires, firefighting should be done from a safe, protected location. Use carbon dioxide (CO_2), dry chemical, or foams to put out hydrogen cyanide fires. Use water sprays to cool fire-exposed containers, protect the personnel attempting to seal the source of the leaking gas, flush spills away from sensitive exposures (heat, sources of ignition, or incompatible chemicals), disperse the vapors, and dilute spills to nonflammable mixtures.

Autoignition Temp: 1000 xF (538 xC)

Unusual fire or explosion hazards: This gas is extremely poisonous and flammable. Consider evacuation of the incident area in large fires.

Special fire-fighting procedures: Wear a self-contained breathing apparatus (SCBA) with a full facepiece operated in the pressure-demand or positive-pressure mode. Fire fighters must wear a complete set of personal protective equipment to prevent virtually any contact with this deadly poison. They must not have exposed skin surfaces since their skin can absorb fatal amounts of hydrogen cyanide.

MSDS 686 continues on page 3

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SECTION V. REACTIVITY DATA

Chemical incompatibilities: Hydrogen cyanide can react dangerously with acetaldehyde.

Conditions to avoid: Specially trained personnel must handle hydrogen cyanide. Never permit inexperienced workers to handle it. Never expose this material to any heat or ignition sources such as lighted cigarettes or pipes, open flames, or uninsulated heating elements.

Hazardous decomposition Products: Thermal oxidative degradation of hydrogen cyanide can produce carbon dioxide, toxic oxides of nitrogen (N_xO_y), and carbon monoxide (CO). Hydrogen cyanide itself is a very toxic material even when not decomposed during fires.

Stability/Polymerization: Hydrogen cyanide is stable at room temperature during routine operations. Hazardous polymerization cannot occur.

SECTION VI. HEALTH HAZARD INFORMATION

Summary of risks: Inhalation of high concentrations of hydrogen cyanide causes tachypnea (rapid breathing) resulting in increased cyanide intake; then dyspnea, paralysis, convulsions, and respiratory arrest. Death may occur within minutes. Lesser concentrations can cause headache, vertigo, nausea, and vomiting. Concentrations of 270 ppm are immediately fatal; 181 ppm in 10 min are fatal; 135 ppm in 30 min are fatal; 110 to 135 ppm in 1 hr are potentially fatal; 45 to 54 ppm are tolerable for 30 to 60 min without immediate or late effects; and 18 to 36 ppm cause slight symptoms after several hours of exposure.

Medical conditions which may be aggravated by contact: None reported.

Target organs: All body cells.

Primary entry route(s): Inhalation, skin contact/absorption.

Acute effects: Burning sensation in mouth and throat. Initially rapid pulse and high blood pressure followed by decreasing blood pressure and pulse. Cherry-red mucous membranes may be noted. Headache, weakness, mental confusion, nausea, vomiting, shock, convulsions, coma, and possible death.

Chronic effect(s): Enlargement of the thyroid gland, fatigue, weakness, headache, changes in taste and smell, irritation of throat, effort dyspnea, nervous instability, lachrymation, abdominal colic, and precordial pain were reported in workers exposed at concentrations between 4 and 12 ppm for approximately 7 years.

 HEALTH HAZARD INFORMATION continues on page 4

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Date: August, 1989

HEALTH HAZARD INFORMATION continued from page 3

First aid:

Eye contact: Immediately flush, including under the eyelids, gently but thoroughly with flooding amounts of running water for at least 15 min.

Skin contact: Immediately remove all contaminated clothing. After rinsing affected area with flooding amounts of water, wash it with soap and water. Avoid contact with this chemical.

Inhalation: Remove the exposed person to fresh air and support breathing as needed. Have qualified medical personnel administer oxygen as required.

Ingestion: Never induce vomiting or perform mouth-to-mouth respiration! Provide 100% oxygen as soon as possible. Institute gastric lavage after endotracheal intubation.

Carcinogenicity: Neither the NTP, IARC, nor OSHA lists hydrogen cyanide as a carcinogen.

After first aid, get appropriate in-plant, paramedic, or community medical attention and support. Seek prompt medical assistance for further observation and treatment. Physician's Note: Treat all exposures as life-threatening emergenies. An antidote to hydrogen cyanide is sodium nitrite and sodium thiosulfate. Commercially available cyanide poisoning first-aid kits should be purchased. Competent medical personnel should carefully train appropriately selected workers on how to use these kits in emergencies. Several detailed medical treatments are available for cyanide poisoning. After reviewing the specific uses of hydrogen cyanide in their operation, the safety personnel and/or the industrial hygienists should develop a precise emergency first-aid treatment protocol before an incident occurs. Heart monitoring should be instituted.

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Product: HYDROGEN CYANIDE

MSDS No: Genium / 686
Date: August, 1989

SECTION VII. SPILL, LEAK AND DISPOSAL PROCEDURES

Spill / Leak procedures: Design and practice a hydrogen cyanide spill control and countermeasure plan (SCCP). Immediately evacuate the incident area and alert the appropriate local officials to the specifics of the hydrogen cyanide release. When a spill occurs, notify safety personnel, eliminate heat or ignition sources, provide optimum explosion-proof ventilation, and implement the SCCP. Cleanup personnel must wear a complete ensemble of personal protective equipment (Sec. 8), including self-contained breathing apparatus and total body-covering clothes, to prevent skin contact or inhalation. Use nonsparking tools and equipment. Use water sprays to protect personnel attempting to locate and seal the source of the escaping hydrogen cyanide gas.

Waste management / Disposal: Contact your supplier or a licensed contractor for detailed recommendations. Follow applicable Federal, state, and local regulations.

OSHA Designations
Listed as an Air Contaminant (29 CFR 1910.1000, Subpart Z)
EPA Designations
Listed as RCRA Hazardous Waste No. P063 (40 CFR 261.33)
Listed as a CERCLA Hazardous Substance* (40 CFR 302.4), Reportable Quantity (RQ): 10 lb (4.54 kg) [* per CWA, Sec. 311(b)(4) and RCRA, Sec. 3001]
Listed as a SARA Extremely Hazardous Substance (40 CFR 355), Threshold Planning Quantity (TPQ): 100 lb
SARA Toxic Chemical (40 CFR 372.65) [* EPA Form R may apply to your facility; see 40 CFR 372.85 for instructions]

SECTION VIII. SPECIAL PROTECTION INFORMATION

Personal protective equipment:

Goggles: Always wear protective eyeglasses or chemical safety goggles, per OSHA eye- and face-protection regulations (29 CFR 1910.133).

Respirator: Wear a NIOSH-approved respirator if necessary. Follow OSHA respirator regulations (29 CFR 1910.134). For emergency or nonroutine operations (leaks or cleaning reactor vessels and storage tanks), wear an SCBA. Warning: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

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MSDS No: Genium / 026
Date: August, 1989

SPECIAL PROTECTION INFORMATION continued from page 5

Other: Wear impervious gloves, boots, aprons, and gauntlets to prevent prolonged or repeated skin contact.

Workplace considerations:

Ventilation: Provide general and local explosion-proof ventilation systems to maintain airborne concentrations below the OSHA PEL standard (Sec. 2). Local exhaust ventilation is preferred since it prevents contaminant dispersion into the work area by eliminating it at its source (Genium ref. 103).

Safety stations:
Make available in the work area emergency eyewash stations, safety/quick-drench showers, and washing facilities.

Contaminated equipment:
Never wear contact lenses in the work area: soft lenses may absorb, and all lenses concentrate, irritants. Launder contaminated clothing before wearing. Remove this material from your shoes and equipment.

Other: Use hydrogen cyanide in closed-confinement, pressurized engineering systems. Automatic shutoff valves/sensors to the main feed lines are strongly recommended in the event of a catastrophic pressure drop from the rupture of a pressurized HCN pipeline.

Never eat, drink, or smoke in work areas. Practice good personal hygiene after using this material, especially before eating, drinking, smoking, using the toilet, or applying cosmetics.

SECTION IX. SPECIAL PRECAUTIONS

Storage segregation: Store hydrogen cyanide in tightly closed, airtight, moisture-proof containers in a cool, dry, well-ventilated, fireproof area away from heat or ignition sources and incompatible chemicals (Sec. 5). Protect these containers from physical damage; shield them from direct sunlight. Limit access to the storage area to authorized personnel only.

Special handling / storage: Proper stock rotation of hydrogen cyanide is vital for safety. Individual HCN cylinders should not be stored longer than 90 days. Check with your supplier for detailed recommendations concerning proper shelf rotation of stock, and proper dispensing equipment such as valves, flanges, and manifolds.

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Date: August 1989

SPECIAL PRECAUTIONS continued from page 6

Engineering controls: To prevent static sparks, electrically ground and bond all containers, cylinders, and pipelines used in shipping, receiving, or transferring operations in production and storage areas.

Other precautions: Consider installing automatic sensing equipment which alerts workers to airborne concentrations of hydrogen cyanide greater than the 10 ppm ceiling (Sec. 2).

Transportation Data (49 CFR 172.101-2)

DOT Shipping Name: Hydrocyanic acid solution
DOT Hazard Class: Poison A or Poison B
ID No.: UN1613 or NA1051
DOT Label: Poison gas and flammable gas
DOT Packaging Requirements: 49 CFR 173.332, .351

IMO Shipping Name: Hydrogen cyanide
IMO Hazard Class: 6.1
IMO Label: Poison and flammable liquid
IMDG Packaging Group: I
Proper shipping names, hazard classes, labels, and identification numbers vary with the hydrogen cyanide's concentration or strength.

Data source code(s): 1, 6, 7, 84-94, 100, 116, 117, 119, 120, 122

Prepared/revised by: Patrick J. Igoe, BS

August, 1989

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erial Safety Data Sheet
MSDS: 23625 - HYDROGEN SULFIDE
========== 3/25/92

Status: Current Revised: 10/23/90

Formula: H2S Part Number:
Specification: NOAA# 3625 Keyword:
Synonyms:
Stock Items:

Manufacturer
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Supplier
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Physical/Chemical Characteristics

Boiling Point .....:	-76.59 F	
Melting Point .....:	-121.9 F	
Freezing Point .....:		
Pour Point .....:		
Softening Point .....:		
Specific Gravity .....:	0.916	@ -76 Deg F
Vapor Pressure .....:	15200	@ 77.9 Deg F
at Temperature ....:	77.9 F	
Vapor Density .....:		
Percent Volatiles ....:		
Evaporation Rate .....:		
pH .....:		
Molecular Weight .....:	34.08	
Viscosity .....:		
Solubility in Water ..:		

Odor/Appearance/Other Characteristics:

Fire and Explosion Data

Closed Cup Flash Pt. .:	NA	Flammable gas.
Open Cup Flash Point .:		
Fire Point .....:		
Auto Ignition .....:	500 F	
Lower Explosion Limit :	4.3	
Upper Explosion Limit :	45	

Shipping Regulations
UN/NA Number: UN1053
DOT Hazard Class:
Shipping Label: FLAMMABLE GAS
Shipping Name:

Prepared
Preparer's Name & Title:
Preparation Date: 10/01/87

Component(s):
HYDROGEN SULFIDE
OSHA Pel:
ACGIH TLV: 10 ppm
STEL: 15 ppm
Percent of Product: CAS No.: 7783064

Text Section(s)

Full Chemical Name

HYDROGEN SULFIDE
CAS number: 7783064

Registry of Toxic Effects of Chemical Substances

MX1225000

Standard Transportation Commodities Code

4905410

List of synonyms for the chemical

HYDROGEN SULFIDE (H2S)
\DIHYDROGEN MONOSULFIDE
\DIHYDROGEN SULFIDE
\HYDROGEN SULFIDE
\HYDROSULFURIC ACID
\STINK DAMP
\SULFUR DIHYDRIDE
\SULFURETED HYDROGEN
\SULFUR HYDRIDE
\ACIDE SULFHYDRIQUE (FRENCH)
\HYDROGENE SULFURE (FRENCH)
\HYDROGEN SULFIDE (ACGIH,DOT)
\HYDROGEN SULFURIC ACID
\IDROGENO SOLFORATO (ITALIAN)
\RCRA WASTE NUMBER U135
\SCHWEFELWASSERSTOFF (GERMAN)
\SIARKOWODOR (POLISH)
\UN 1053 (DOT)
\ZWAVELWATERSTOF (DUTCH)

DOT label

FLAMMABLE GAS

NFPA

NFPA rating for Health Hazard --
3
NFPA rating for Flammability Hazard --
4
NFPA rating for Reactivity Hazard --
0

General description of a chemical

Hydrogen sulfide is a colorless gas having the odor of rotten eggs. It is shipped as a liquefied gas under its own vapor pressure. One's sense of smell becomes rapidly fatigued in atmospheres containing hydrogen sulfide and hence cannot be counted on to warn of the continued presence of the gas. Contact with the liquid can cause frostbite. The gas is heavier than air and a flame can flash back to the source of leak very easily. Under fire conditions cylinders and tank cars may violently rupture and rocket. It is soluble in water. ((C)AAR, 1986)

Fire and Explosion Hazards Information

Fire and explosion hazards --
A very flammable gas. Compound is heavier than air and may travel a considerable distance to source of ignition and flash back. It forms explosive mixtures with air over a wide range. Also reacts explosively with bromine pentafluoride, chlorine trifluoride, nitrogen triiodide, nitrogen trichloride, oxygen difluoride, and phenyl diazonium chloride. Avoid physical damage to containers; sources of ignition; storage near nitric acid, strong oxidizing materials, and corrosive liquids or gases. Incompatible with metals. When heated to decomposition, it emits highly toxic fumes of oxides of sulfur. (EPA, 1986)
Fire fighting techniques --
For small fires let burn unless leak can be stopped immediately. For large fires, use water spray, fog or foam. Stop flow of gas. Use water to keep fire-exposed containers cool and to protect men effecting the shut-off. Move container from fire area. Stay away from ends of tanks. Withdraw immediately in case of rising sound from venting safety device or any discoloration on tank due to fire. Cool containers with water using unmanned device until well after fire is out. (EPA, 1986)

Protective clothing recommendations

Wear positive pressure breathing apparatus and special protective clothing. (EPA, 1986)

Compatibility

Compatibility with Butyl Rubber --
Good Resistance/Limited Data.
Compatibility with chlorinated polyehtylene --
Good Resistance/Limited Data.
Compatibility with neoprene --
Good Resistance/Good Data.
Compatibility with polyurethane --
Poor Resistance/Limited Data.
Compatibility with polyvinyl chloride --
Good Resistance/Good Data.
Compatibility with natural rubber --
Poor Resistance/Limited Data.
Compatibility with styrene/butadiene coated fabric --
Good Resistance/Limited Data.

Evacuation information

Evacuate area endangered by gas. Keep unnecessary people away; stay upwind; keep out of low areas. Isolate for one-half mile in all directions if tank car or truck is involved in fire. If a spill or leak from a drum or smaller container or a small leak from a tank, then isolate 120 feet in all directions. If a large spill from a tank or from many containers or drums, etc., first isolate 240 feet in all directions. Then evacuate in a downwind direction, an area 0.6 miles wide and 0.9 miles long. Isolate area until gas has dispersed. (EPA, 1986)

Non-Fire response information

Keep sparks, flames, and other sources of ignition away. Keep material out of water sources and sewers. Attempt to stop leak if without hazard. Use water spray to knock-down vapors. Land spill: Dike surface flow using soil, sand bags, foamed polyurethane, or foamed concrete. Absorb bulk liquid with fly ash or cement powder. Neutralize with agricultural lime (slaked lime), crushed limestone, or sodium bicarbonate. Water spill: Neutralize with agricultural lime (slaked lime), crushed limestone, or sodium bicarbonate. Air spill: Apply water spray or mist to knock down vapors. Vapor knockdown water is corrosive or toxic and should be diked for containment. ((C)AAR, 1986)

Health hazard information

Exposure to very high concentrations causes immediate death. Also death or permanent injury may occur after very short exposure to small quantities. It acts directly upon the nervous system resulting in paralysis of respiratory centers. Signs and Symptoms of Exposure: Contact with eyes causes painful conjunctivitis, sensitivity to light, tearing, and clouding of vision. Inhalation of low concentrations causes a runny nose with a loss of smelling sense, labored breathing, and shortness of breath. Direct contact with skin causes pain and redness. Other symptoms of exposure include profuse salivation, nausea, vomiting, diarrhea, giddiness, headache, dizziness, confusion, rapid beathing, rapid heart rate, sweating, weakness, sudden collapse, unconsciousness and death due to respiratory paralysis. (EPA, 1986)

First aid information

Move victim to fresh air; call emergency medical care. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact with material, immediately flush skin or eyes with running water for at least 15 minutes. Keep victim quiet and maintain normal body temperature. Effects may be delayed; keep victim under observation. (EPA, 1986)

Fire and Explosion Data

Flash point of chemical --
Not Applicable. Flammable gas. (USCG, 1985)
Lower explosive limit --
4.3 % (EPA, 1986)
Upper explosive limit --
45 % (EPA, 1986)
Auto-ignition temperature --
500 Deg F (USCG, 1985)

Physical / Chemical Characteristics

Melting point --
-121.9 Deg F (EPA, 1986)
Vapor pressure --
15200 mm Hg @ 77.9 Deg F (EPA, 1986)
Specific gravity of vapor form --
1.19 (EPA, 1986)
Specific gravity of liquid form --
0.916 @ -76 Deg F (EPA, 1986)
Boiling point --

-76.59 Deg F (EPA, 1986)

Molecular weight --

34.08 (EPA, 1986)

Exposure Limits

NIOSH Immediately Dangerous to Life and Health value --

300 ppm (NIOSH, 1987)

Time Weighted Average of the Threshold Limit Value --

10 ppm ((C)ACGIH, 1986)

Short Term (15 minute) Exposure limit of the Threshold Limit Value --

15 ppm ((C)ACGIH, 1986)

End of MSDS

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Schenectady, NY 12303-1836 USA
(518) 377-8854

Material Safety Data Sheets Collection:

Sheet No. 440
Methane

Issued: 7/80 Revision: A, 8/89

Section 1. Material Identification

Methane Description: Widely distributed in nature, methane comprises 0.00022% by volume of the earth's atmosphere. American natural gas is mostly methane (85%). At temperatures greater than 2012 °F (1100 °C), pure carbon combines with pure hydrogen to form methane. Above 2732 °F (1500 °C), the amount of methane produced increases with temperature. Obtained from sodium acetate and sodium hydroxide or from aluminum carbide and water. Commercially prepared from natural gas or by fermentation of cellulose and sewage sludge. Constituent of illuminating and cooking gas. Used in the manufacture of hydrogen, hydrogen cyanide, ammonia, acetylene, formaldehyde, and many other organics.
Other Designations: Fire damp; marsh gas; methyl hydride; CH_4; CAS No. 0074-82-8.
Manufacturer: Contact your supplier or distributor. Consult the latest *Chemicalweek Buyers' Guide* (Genium ref. 73) for a suppliers list.

R 1
I -
S -
K 4

NFPA

HMIS
H 1
F 4
R 0
PPG*
* Sec. 8

Section 2. Ingredients and Occupational Exposure Limits

Methane, ca 100%*

OSHA PEL	ACGIH TLV, 1988-89	NIOSH REL	Toxicity Data†
None established	None established	None established	Not listed

* Check with your supplier to determine the exact composition of the purchased methane. Possible contaminants are ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), higher molecular weight alkanes, carbon dioxide (CO_2), nitrogen (N_2), and oxygen(O_2).
† Monitor NIOSH, *RTECS* (PA1490000), for future toxicity data.

Section 3. Physical Data

Boiling Point: -259 °F (161.6 °C)
Vapor Density (Air = 1): 0.544 at 32 °F (0 °C)
Molecular Weight: 16 g/mol
Water Solubility: Slight*
Melting Point: -296.5 °F (-182.5 °C)

Appearance and Odor: A colorless, odorless, tasteless, extremely flammable gas. Commercial methane's trace amounts of a suitable mercaptan compound give it natural gas's familiar rotten egg smell.

*Soluble in alcohol and ether.

Section 4. Fire and Explosion Data

Flash Point: -213 °F (-136.11 °C)	Autoignition Temperature: 999 °F (537 °C)	LEL: 5% v/v*	UEL: 15% v/v*

Extinguishing Media: Methane's extreme flammability, extensive explosibility range, and very low flash point represent dangerous fire and explosion risks. *Treat any fire situation involving rapidly escaping and burning methane gas as an emergency.* Extinguish methane fires by shutting off the source of the gas. Use water sprays to cool fire-exposed containers and to protect the personnel attempting to seal the source of the escaping gas.
Unusual Fire or Explosion Hazards: Methane gas is very flammable with an extensive explosibility range. The best fire-fighting technique may be simply to let the burning gas escape from the pressurized cylinder, tank car, or pipelines. Never extinguish the burning gas without first locating and sealing its source. Otherwise, the still leaking gas could explosively re-ignite without warning and cause more damage than if it burned itself out.
Special Fire-fighting Procedures: Wear a self-contained breathing apparatus (SCBA) with a full facepiece operated in the pressure-demand or positive-pressure mode.

* The loudest methane-air explosions occur when 1 volume of methane is mixed with 10 volumes of air (or 2 volumes of oxygen). **Warning:** Air with more than 14% by volume methane burns *noiselessly*. Methane burns with a pale, faintly luminous, not always easily detected flame.

Section 5. Reactivity Data

Stability/Polymerization: Methane is stable at room temperature in closed, pressurized containers during routine operations. Hazardous polymerization cannot occur.
Chemical Incompatibilities: Genium reference 84 reports that methane can react violently with bromine pentafluoride, chlorine, chlorine dioxide, nitrogen trifluoride, liquid oxygen, and oxygen difluoride.
Conditions to Avoid: Never expose methane to ignition sources such as open flame, lighted cigarettes or pipes, uninsulated heating elements, or electrical or mechanical sparks. Prevent any accidental or uncontrollably rapid release of methane gas from high-pressure cylinders, tank cars, or pipelines.
Hazardous Products of Decomposition: Thermal oxidative degradation of methane can produce carbon dioxide and toxic carbon monoxide (CO).

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Section 6. Health Hazard Data

Carcinogenicity: Neither the NTP, IARC, nor OSHA lists methane as a carcinogen. **Summary of Risks:** As a simple asphyxiant, methane does not cause significant physiological responses, but it can displace the minimum required atmospheric oxygen level. Significant displacement results in an oxygen-deficient atmosphere with no adequate warning properties. Asphyxiation can occur especially in confined, poorly ventilated, undisturbed spaces infrequently entered by workers. Frostbite (cryogenic damage) can result from contact with liquid methane's extremely low temperature. **Medical Conditions Aggravated by Long-Term Exposure:** None reported. **Target Organs:** None reported. **Primary Entry:** Inhalation. **Acute Effects:** The initial symptoms of simple asphyxiant gases's effects are rapid respiration and air hunger, diminished mental alertness, and impaired muscular coordination. Continuing lack of oxygen causes faulty judgement, depression of all sensations, rapid fatique, emotional instability, nausea, vomiting, prostration, unconsciousness, and finally, convulsions, coma, and death. **Chronic Effects:** None reported.

FIRST AID

Skin: (Liquid methane): Promptly flush the affected area with lots of tepid/lukewarm water to reduce freezing of tissues. Never apply direct heat to frostbitten areas. Loosely apply dry, bulky dressings to protect the area from further injury. Get treatment from qualified medical personnel. **Inhalation:** Rescuers must consider their own safety when entering confined, poorly ventilated, oxygen-deficient areas. Self-contained breathing equipment must be readily available. Rescuers must use nonsparking tools and equipment; e.g., floodlights lowered into any incident area must be electrically grounded and bonded, shatter-resistant, and sparkproof. **After first aid, get appropriate in-plant, paramedic, or community medical attention and support for inhalation exposures in oxygen-deficient atmospheres.** Seek prompt medical assistance for further observation and treatment.

Section 7. Spill, Leak, and Disposal Procedures

Spill/Leak: *Design and practice a methane spill control and countermeasure plan (SCCP).* When a leak occurs, notify safety personnel, eliminate heat and ignition sources, evacuate unnecessary personnel, provide maximum explosion-proof ventilation, and implement the SCCP. Use only nonsparking tools and equipment. Locate and seal the source of the leaking gas. Use water sprays to protect the personnel attempting this shutoff. Large methane releases can result in spectacular explosions. If attempts to shut off the leaking gas are unsuccessful, evacuate the likely explosion area. **Disposal:** Contact your supplier or a licensed contractor for detailed recommendations. Follow applicable Federal, state, and local regulations. Remove leaking or defective cylinders to a safe, outside, posted, discharge location. Let the methane gas discharge at a moderate rate. When it is empty, return the cylinder to the supplier after it is properly tagged, labelled, or stenciled MT (empty) or defective.

OSHA Designations

Air Contaminant (29 CFR 1910.1000, Subpart Z): Not listed

EPA Designations

RCRA Hazardous Waste (40 CFR 261.33): Not listed
CERCLA Hazardous Substance (40 CFR 302.4): Not listed
SARA Extremely Hazardous Substance (40 CFR 355): Not listed
SARA Toxic Chemical (40 CFR 372.65): Not listed

Section 8. Special Protection Data

Goggles: Wear protective eyeglasses or chemical safety goggles, per OSHA eye- and face-protection regulations (29 CFR 1910.133). **Gloves:** To prevent skin contact, workers handling liquid methane should wear appropriate insulating gloves, safety glasses, and splash aprons, as required by the particular work conditions. **Respirator:** Wear a NIOSH-approved respirator if necessary. Follow OSHA respirator regulations (29 CFR 1910.134). For emergency or nonroutine operations (spills or cleaning reactor vessels and storage tanks), wear an SCBA. **Warning:** Air-purifying respirators do *not* protect workers in oxygen-deficient atmospheres; use self-contained breathing equipment there. **Ventilation:** Provide general and local explosion-proof ventilation systems to maintain airborne concentrations below the 5% v/v LEL (Sec. 4). Local exhaust ventilation is preferred since it prevents methane dispersion into the work area by eliminating it at its source (Genium ref. 103). Give special attention to proper ventilation of enclosed areas. **Safety Stations:** Make available in the work area emergency eyewash stations, safety/quick-drench showers, washing facilities, fire extinguishers, and oxygen bottles for emergency first-aid. **Contaminated Equipment:** Never wear contact lenses in the work area: soft lenses may absorb, and all lenses concentrate, irritants. Launder contaminated clothing before wearing. Remove this material from your shoes and equipment. **Other:** If appropriate, consider installing automatic sensing equipment that warns workers of oxygen-deficient atmospheres or of potentially explosive air-gas mixtures. All engineering systems in any methane gas storage, handling, or processing area must be explosion-proof so they have no spark potential or hot spots. Pressurized systems must use only approved valves, manifolds, flanges, and flame arrestors. **Comments:** Methane gas presents dangerous fire, explosion, and reactivity risks. Regularly inspect and service all the piping systems which transport methane gas in production and storage areas. Before use, thoroughly test methane lines with nitrogen gas for leaking, especially in enclosed areas.

Section 9. Special Precautions and Comments

Storage Requirements: Store methane in closed, pressurized cylinders, tank cars, pipelines, or other containers in a cool, dry, well-ventilated, fireproof area away from heat and ignition sources and incompatible chemicals (Sec. 5). Protect these containers from physical damage and heat. Shield them from direct sunlight. **Special Handling/Storage:** Electrically ground and bond all containers, tanks, cylinders, tank cars and pipelines used in methane shipping, receiving, or transferring operations. Never smoke in any work area where the possibility of exposure to methane gas (fire hazard) exits. Recommended storage containers include steel.

Transportation Data (49 CFR 172.101-2)

DOT Shipping Name: Methane
DOT Hazard Class: Flammable gas
DOT ID No.: UN1971
DOT Label: Flammable gas
DOT Packaging Requirements: 49 CFR 173.302
DOT Packaging Exceptions: 49 CFR 173.306

IMO Shipping Name: Methane, compressed
IMO Hazard Class: 2.1
IMO Label: Flammable gas

***MSDS Collection* References:** 1, 6, 7, 84-94, 100, 116, 117, 119, 120, 122

Prepared by: PJ Igoe, BS; **Industrial Hygiene Review:** DJ Wilson, CIH; **Medical Review:** MJ Hardies, MD

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Material Safety Data Sheet

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GENIUM PUBLISHING CORP.

No. 310
METHYLENE CHLORIDE
(Revision F)

Issued: September 1985
Revised: November 1988

SECTION 1. MATERIAL IDENTIFICATION

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Material Name: METHYLENE CHLORIDE

Description (Origin/Uses): Used widely in paint removers, as a solvent for plastics, as a degreasing agent, in propellant mixtures for aerosol sprays, and as a blowing agent in foams.

Other Designations: Dichloromethane; Freon 30®; Methane Dichloride; Methylene Bichloride; Methylene Dichloride; CH_2Cl_2; CAS No. 0075-09-2

Manufacturer: Contact your supplier or distributor. Consult the latest edition of the *Chemicalweek Buyers' Guide* (Genium ref. 73) for a list of suppliers.

HMIS
H 2
F 1
R 0
PPG*
*See sect. 8

R 1
I 3
S 3
K 1

NFPA

SECTION 2. INGREDIENTS AND HAZARDS/EXPOSURE LIMITS

Methylene Chloride, ca 100%

OSHA PEL
8-Hour TWA: 500 ppm
Ceiling: 1000 ppm Acceptable Maximum Peak above the Ceiling: 2000 ppm for 5 Minutes in Any 2-Hour Period

ACGIH TLV, 1988-89
TLV-TWA: 50 ppm, 175 mg/m³
(Adopted 1988-89)

Toxicity Data*
Rat, Oral, LD_{50}: 2136 mg/kg
Human, Inhalation, TC_{Lo}: 500 ppm (8 Hours)

*See NIOSH, *RTECS* (PA8050000), for additional data with references to irritative, reproductive, mutagenic, and tumorigenic effects.

SECTION 3. PHYSICAL DATA

Boiling Point: 103.55°F (39.75°C) at 76 Torrs
Melting Point: -142°F (-96.7°C)
Vapor Density (Air = 1): 2.9
Vapor Pressure: 440 Torrs at 77°F (25°C)
Molecular Weight: 84.94 Grams/Mole
Solubility in Water (%): 1% by Weight
Specific Gravity (H_2O = 1): 1.3255 at 68°F (20°C)
% Volatile by Volume: Ca 100

Appearance and Odor: A clear, colorless, volatile liquid; distinctive, penetrating, ethereal odor. The odor will not serve as a useful warning property because concentrations of 100 ppm are not easily perceptible. Most persons can detect this odor at above 300 ppm.

SECTION 4. FIRE AND EXPLOSION DATA

Flash Point*	Autoignition Temperature: 1033°F (556°C)	LEL: 12% v/v	UEL: 19% v/v

Extinguishing Media: *Methylene chloride is not flammable under ordinary conditions. However, flammable vapor-air mixtures can form at approximately 212°F (100°C). Use water spray to cool fire-exposed containers and to flush spills away from exposures. Use extinguishing agents that will put out the surrounding fire. **Unusual Fire or Explosion Hazards:** Methylene chloride vapor is heavier than air and may collect and concentrate in low-lying, confined spaces. The high vapor pressure of methylene chloride means that when it is spilled, its vapor concentration in air can increase rapidly. If this vapor is heated, an explosion hazard is associated with the vapor-air mixture. Containers of this material may rupture violently if they are involved in fires. **Special Fire-fighting Procedures:** Wear a self-contained breathing apparatus (SCBA) with a full facepiece operated in the pressure-demand or positive-pressure mode.

SECTION 5. REACTIVITY DATA

Stability/Polymerization: Methylene chloride is stable in closed containers during routine operations. Hazardous polymerization cannot occur. **Chemical Incompatibilities:** Methylene chloride can react dangerously with nitrogen tetroxide, liquid oxygen, potassium, sodium, sodium-potassium alloys, lithium, potassium hydroxide with N-methyl-N-nitroso urea, potassium *t*-butoxide, and finely powdered aluminum and magnesium. **Conditions to Avoid:** Avoid all exposure to sources of ignition, heat, and incompatible chemicals. Prolonged exposure to water may cause hydrolysis to highly corrosive hydrochloric acid when the temperature is above 140°F (60°C). In oxygen-enriched atmospheres or when heated (>212°F [100°C]), methylene chloride vapor can be readily ignited. **Hazardous Products of Decomposition:** Exposure to high temperature (from open flame, hot surfaces, uninsulated steam lines, welding arcs, etc.) can produce toxic and corrosive thermal-oxidative products of decomposition such as hydrogen chloride, carbon monoxide, and even small quantities of phosgene gas, which is extremely poisonous.

SECTION 6. HEALTH HAZARD INFORMATION

Carcinogenicity: Methylene chloride is listed as a suspected human carcinogen by the ACGIH (which classifies it as a group A2 carcinogen). **Summary of Risks:** Accidental contact of liquid methylene chloride with skin or eyes causes painful irritation and possible burns if not promptly removed. Exposure by way of contaminated gloves, clothing, or paint remover formulations can produce these same irritant effects. Long-term exposure to mild or moderate doses of methylene chloride may cause a delayed (24 to 48 hours) onset of dizziness, headache, mental confusion, slurred speech, double vision, and sleeplessness. Medical recovery can be slow. Overexposure to methylene chloride can cause elevated levels of carboxy hemoglobin in the blood (this same effect results from overexposure to carbon monoxide). **Medical Conditions Aggravated by Long-Term Exposure:** None reported. **Target Organs:** Skin, eyes, respiratory system, CNS, liver, kidneys, and blood. **Primary Entry:** Inhalation, skin contact/absorption. **Acute Effects:** Headache, giddiness, stupor, irritability, fatigue, tingling in the limbs, and narcosis that is not usually fatal if the exposure is terminated before anesthetic death occurs. **Chronic Effects:** The ACGIH classification of this material as a suspected human carcinogen implies that cancer is a possible effect of chronic exposure to methylene chloride. **FIRST AID: Eyes.** Immediately flush eyes, including under the eyelids, gently but thoroughly with

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SECTION 6. HEALTH HAZARD INFORMATION, cont.

flooding amounts of running water for at least 15 minutes. **Skin.** Rinse the affected area with flooding amounts of water and then wash it with soap and water. **Inhalation.** Remove the exposed person to fresh air; restore and/or support his or her breathing as needed. Have qualified medical personnel administer oxygen as required. **Note to Attending Physician:** Do not administer adrenalin. **Ingestion.** Unlikely. Should this type of exposure occur, do not induce vomiting because of the danger of aspiration. If spontaneous vomiting should occur, position the exposed person's head below his or her trunk to resist aspiration. **Get medical help (in plant, paramedic, community) for all exposures.** Seek prompt medical assistance for further treatment, observation, and support after first aid. **Note to Physician:** Absorbed methylene chloride is stored in body fat and metabolizes to carbon monoxide. This produced carbon monoxide increases and sustains carboxyhemoglobin levels in the blood, which concommitantly reduces the oxygen-carrying capacity of the blood. NIOSH advises preplacement and annual medical exams that empnasize liver, kidney, eye, skin, CNS, and respiratory system functions and a complete blood count. Simultaneous exposure to tobacco smoke, alcohol, and carbon monoxide, along with heavy manual labor, increases the body burden of a worker as well as the toxic hazards of the methylene chloride. In significant exposures, serum methylene chloride levels are of no clinical importance. Neurologic and hepatic status as well as carboxy hemoglobin should be monitored.

SECTION 7. SPILL, LEAK, AND DISPOSAL PROCEDURES

Spill/Leak: Notify safety personnel, evacuate unnecessary personnel, eliminate all sources of ignition immediately, and provide adequate explosion-proof ventilation. Cleanup personnel need protection against this liquid's contact with the skin or eyes as well as inhalation of its vapor. Contain large spills and collect waste or absorb it with an inert material such as sand, earth, or vermiculite. Use nonsparking tools to place waste liquid or absorbent into closable containers for disposal. Keep waste out of sewers, watersheds, and waterways. **Waste Disposal:** Contact your supplier or a licensed contractor for detailed recommendations. Follow Federal, state, and local regulations.

OSHA Designations
Listed as an Air Contaminant (29 CFR 1910.1000 Subpart Z).
EPA Designations (40 CFR 302.4)
RCRA Hazardous Waste, NO. U080
CERCLA Hazardous Substance, Reportable Quantity: 1000 lbs (454 kg), per the Clean Water Act (CWA), § 307 (a), and the Resource Conservation and Recovery Act (RCRA), § 3001.

SECTION 8. SPECIAL PROTECTION INFORMATION

Goggles: Always wear protective eyeglasses or chemical safety goggles. Where splashing is possible, wear a full face shield. Follow OSHA eye- and face-protection regulations (29 CFR 1910.133). **Respirator:** Use a NIOSH-approved respirator per Genium reference 88 for the maximum-use concentrations and/or exposure limits cited in section 2. Follow OSHA respirator regulations (29 CFR 1910.134). For emergency or nonroutine operations (spills or cleaning reactor vessels and storage tanks), wear an SCBA. **Warning:** Air-purifying respirators will *not* protect workers in oxygen-deficient atmospheres. **Other:** Wear impervious neoprene, PVA, or Viton gloves, boots, aprons, and gauntlets, etc., to prevent any skin contact with liquid methylene chloride. **Ventilation:** Install and operate general and local maximum, explosion-proof ventilation systems powerful enough to maintain airborne levels of acetone below the exposure limits cited in section 2. Local exhaust ventilation is preferred because it prevents dispersion of the contaminant into the general work area by eliminating it at its source. Consult the latest edition of Genium reference 103 for detailed recommendations. Floor or sump ventilation may be necessary. **Safety Stations:** Make emergency eyewash stations, safety/quick-drench showers, and washing facilities available in work areas. **Contaminated Equipment:** Contact lenses pose a special hazard; soft lenses may absorb irritants, and all lenses concentrate them. Do *not* wear contact lenses in any work area. Remove contaminated clothing and launder it before wearing it again; clean this material from shoes and equipment. **Other:** Because the health effects of carbon monoxide and methylene chloride are additive (see sect. 6), workplaces should be equipped with automatic sensing equipment that identifies workroom atmospheric levels of both of these materials. **Comments:** Practice good personal hygiene; always wash thoroughly after using this material and before eating, drinking, smoking, using the toilet, or applying cosmetics. Keep it off your clothing and equipment. Avoid transferring it from your hands to your mouth while eating, drinking, or smoking. Do *not* eat, drink, or smoke in any work area. Do not inhale methylene chloride vapor.

SECTION 9. SPECIAL PRECAUTIONS AND COMMENTS

Storage/Segregation: Store methylene chloride in closed, moisture-proof containers in a cool, dry, well-ventilated area away from sources of ignition, strong oxidizers, caustics, and incompatible chemicals (see sect. 5). Protect containers from physical damage. **Special Handling/Storage:** Prevent moist air from entering storage containers. Provide ventilation at the floor level in storage areas because methylene chloride vapor is denser than air. Installation of a dryer and a safety seal on each tank is recommended. Aluminum is not recommended for use as a storage material; appropriate storage materials include galvanized iron, black iron, or steel. **Engineering Controls:** Make sure all engineering systems (production, transportation) are of maximum explosion-proof design. Electrically ground and bond all containers and pipelines used in shipping, transferring, reacting, production, and sampling operations to prevent generating static sparks.

Transportation Data (49 CFR 172.101-2)
DOT Shipping Name: Dichloromethane *or* Methylene Chloride
DOT Hazard Class: ORM-A
ID No. UN1593
DOT Packaging Requirements: 49 CFR 173.605
DOT Packaging Exceptions: 49 CFR 173.505

IMO Shipping Name: Dichloromethane
IMO Hazard Class: 6.1
IMO Label: Saint Andrew's Cross (X)*
IMDG Packaging Group: III

*Harmful-Stow away from Foodstuffs.

References: 1, 26, 38, 84-94, 100, 116, 117, 120, 122.

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Industrial Hygiene Review: DJ Wilson, CIH
Medical Review: MJ Hardies, MD

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Material Safety Data Sheet

From Genium's Reference Collection
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GENIUM PUBLISHING CORP.

No. 359
ETHYLENE DICHLORIDE
(Formerly 1,2-Dichloroethane)
(Revision C)
Issued: November 1978
Revised: August 1987

SECTION 1. MATERIAL IDENTIFICATION

23

CHEMICAL NAME: ETHYLENE DICHLORIDE (Changed to reflect common industrial practice)
DESCRIPTION (Origin/Uses): Made from acetylene and HCl. Used as a degreaser, a scavenger in leaded gasoline, as an intermediate in the manufacture of vinyl chloride, in paint removers, in wetting and penetration agents, in ore flotation processes, as a fumigant, and as a solvent for fats, oils, waxes, and gums.
OTHER DESIGNATIONS: 1,2-Dichloroethane; *sym*-Dichloroethane; Dutch Liquid; Dutch Oil; EDC; Ethane Dichloride; Ethylene Chloride; 1,2-Ethylene Dichloride; Glycol Dichloride; $C_2H_4Cl_2$; NIOSH *RTECS* KI0525000; CAS #0107-06-2
MANUFACTURERS/SUPPLIERS: Available from several suppliers, including: Dow Chemical USA, 2020 Dow Center, Midland, MI 48640; Telephone: (517) 636-1000

COMMENTS: Ethylene dichloride is a flammable, toxic liquid.

HMIS			
H	1	R	1
F	3	I	4
R	0	S	2
PPE*		K	4

* See Sect. 8

SECTION 2. INGREDIENTS AND HAZARDS

Ingredients	%	HAZARD DATA
Ethylene Dichloride, CAS #0107-06-2; NIOSH *RTECS* #KI0525000 H H Cl – C – C – Cl H H *The maximum allowable peak concentration (above the ceiling level value) of ethylene dichloride is 200 ppm for 5 minutes in any 3-hour period. COMMENTS: Additional data concerning toxic doses and tumorigenic, reproductive, and mutagenic effects is listed (with references) in the NIOSH *RTECS* 1983-84 supplement, pages 865-66.	100	ACGIH Values 1987-88 TLV-TWA: 10 ppm, 40 mg/m^3 OSHA PEL* 1986-87 8-Hr TWA: 50 ppm; Ceiling: 100 ppm (15 Min.) NIOSH REL 1986-87 10-Hr TWA: 1 ppm Ceiling: 2 ppm (15 Min.) Toxicity Data Man, Inhalation, TC_{Lo}: 4000 ppm/1 Hr Human, Oral, TD_{Lo}: 428 mg/kg Man, Oral, TD_{Lo}: 892 mg/kg Man, Oral, LD_{Lo}: 714 mg/kg Rat, Oral, LD_{50}: 670 mg/kg

SECTION 3. PHYSICAL DATA

Boiling Point ... 182.3°F (83.5°C)
Vapor Pressure ... 87 Torr at 77°F (25°C)
Water Solubility ... Soluble in about 120 Parts Water
Vapor Density (Air = 1) ... 3.4
Evaporation Rate (n-BuAc = 1) ... Not Listed
Specific Gravity ... 1.2569 at 69°F (20°C)
Freezing Point ... -31.9°F (-35.5°C)
Molecular Weight ... 98.96 Grams/Mole

Appearance and odor: Colorless, clear liquid. Sweet, chloroformlike odor is typical of chlorinated hydrocarbons. The recognition threshold (100% of test panel) for ethylene dichloride is 40 ppm. Odor detection probably indicates an excessive exposure to vapor. High volatility and flammability, coupled with its toxicity and carcinogenic potential, make this material a major health hazard.
COMMENTS: Ethylene dichloride is miscible with alcohol, chloroform, and ether.

SECTION 4. FIRE AND EXPLOSION DATA

Flash Point and Method	Autoignition Temperature	Flammability Limits in Air	LOWER	UPPER
See Below	775°F (413°C)	% by Volume	6.2	15.9

EXTINGUISHING MEDIA: Use chemical, carbon dioxide, alcohol foam, water spray/fog, or dry sand to fight fires involving ethylene dichloride. Direct water sprays may be ineffective extinguishing agents, but they may be successfully used to cool fire-exposed containers. Use a smothering effect to extinguish fires involving this material. UNUSUAL FIRE/EXPLOSION HAZARDS: Ethylene dichloride is a dangerous fire and explosion hazard when exposed to sources of ignition such as heat, open flames, sparks, etc. Its vapors are heavier than air and can flow along surfaces to distant, low-lying sources of ignition and flash back. If it is safe to do so, remove this material from the fire area. Ethylene dichloride burns with a smoky flame.
SPECIAL FIRE-FIGHTING PROCEDURES: Wear a self-contained breathing apparatus with a full facepiece operated in a pressure-demand or another positive-pressure mode.
COMMENTS: Flash Point and Method: 56°F (13°C) CC; 65°F (18°C) OC.
OSHA Flammability Class (29 CFR 1910.106): IB. DOT Flammability Class (49 CFR 173.115): Flammable Liquid

SECTION 5. REACTIVITY DATA

Ethylene dichloride is stable. Hazardous polymerization cannot occur.

CHEMICAL INCOMPATIBILITIES include strong oxidizing agents. Explosions have occurred with mixtures of this material and liquid ammonia or dimethylaminopropylamine. Finely divided aluminum or magnesium metal may be hazardous in contact with ethylene dichloride.
CONDITIONS TO AVOID: Eliminate sources of ignition such as excessive heat, open flames, or electrical sparks, particularly in low-lying areas, because the explosive, heavier-than-air vapors will concentrate there.
PRODUCTS OF HAZARDOUS DECOMPOSITION can include vinyl chloride, chloride fumes, and phosgene. Phosgene is an extremely poisonous gas. Products of thermal-oxidative degradation (i.e., fire conditions) must be treated with appropriate caution.

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SECTION 6. HEALTH HAZARD INFORMATION

Ethylene dichloride is listed as an anticipated human carcinogen by the NTP and as a probable human carcinogen (Group 2B), by the IARC. It was found to be an animal-positive carcinogen by the IARC. NCI reported positive results (mouse, rat) from its carcinogenesis bioassay. SUMMARY OF RISKS: Ethylene dichloride is considered to be one of the more toxic of the common chlorinated hydrocarbons. Deaths from accidental ingestion of this material have been reported. Inhalation of vapors reportedly caused three fatalities. Excessive inhalation of ethylene dichloride vapors can cause respiratory irritation, intoxication, narcotic and anesthetic effects, vomiting, dizziness, depression, and diarrhea. The hepatoxic (injurious to liver) effects of this material are significant. The systemic effects from overexposure can appear in the liver, kidneys, digestive tract, blood, lungs, adrenal glands, and the central nervous system. Tests on animals have revealed reproductive failure and fetal resorption. There may be increased risk to nursing infants of exposed mothers. TARGET ORGANS: Central nervous system, eyes, kidneys, liver, heart, adrenal glands, and skin. PRIMARY ENTRY: Inhalation, absorption through skin, oral, or eye contact. ACUTE EFFECTS: Skin contact causes irritation, defatting, and, if repeated or prolonged, burning. Eye contact causes irritation and serious injury (clouding of the cornea) if it is not removed promptly. CHRONIC EFFECTS: Injuries to the liver (hepatoxicity) and kidneys, weight loss, low blood pressure, jaundice, oliguria (reduced excretion of urine), or anemia. MEDICAL CONDITIONS AGGRAVATED BY LONG-TERM EXPOSURE: Persons taking anticoagulants could experience an increase in tendency to bleed. Persons taking insulin face an increased risk of lowered blood sugar. FIRST AID: Be prepared to restrain a hyperactive victim. EYE CONTACT: Flush eyes, including under the evelids, gently but thoroughly with plenty of running water for at least 15 minutes. Get medical help.* SKIN CONTACT: Immediately flush the affected area with water. Wash thoroughly with soap and water. Remove and launder contaminated clothing before wearing it again; clean material from shoes and equipment. Get medical help.* INHALATION: Remove victim to fresh air; restore and/or support his breathing as needed. Get medical help.* INGESTION: Never give anything by mouth to someone who is unconscious or convulsing. Rinse victim's mouth with water. Oxygen and artificial respiration may be needed. Get medical help.* * GET MEDICAL ASSISTANCE = IN PLANT, PARAMEDIC, COMMUNITY. Get prompt medical assistance for further treatment, observation, and support after first aid.

SECTION 7. SPILL, LEAK, AND DISPOSAL PROCEDURES

SPILL/LEAK: Before using ethylene dichloride, it is essential that proper emergency procedures be established and made known to all personnel involved in handling it. Notify safety personnel of ethylene dichloride spills or leaks and implement containment procedures. Remove and eliminate all possible sources of ignition such as heat, sparks, and open flames from the area. Cleanup personnel should use protection against inhalation of vapors and contact with liquid. Contain spills by using an absorbent material such as dry sand or vermiculite. Use nonsparking tools to mix waste material thoroughly with absorbent and place it in an appropriate container for disposal. Flush trace residues with large amounts of water. Do not flush waste to sewers or open waterways. WASTE DISPOSAL: Consider reclamation, recycling, or destruction rather than disposal in a landfill. Waste may be burned in an approved incinerator equipped with an afterburner and a scrubber. Follow Federal, state, and local regulations.

Ethylene dichloride is designated as a hazardous substance by the EPA (40 CFR 116.4). Ethylene dichloride is reported in the 1983 EPA TSCA Inventory.

EPA Hazardous Waste Number (40 CFR 261.33): U077

EPA Reportable Quantity (40 CFR 117.3): 5000 lbs (2270 kgs)

Aquatic Toxicity Rating, TLm 96: 1000 - 100 ppm

SECTION 8. SPECIAL PROTECTION INFORMATION

GOGGLES: Always wear protective eyeglasses or chemical safety goggles. Ethylene dichloride is particularly harmful to the eyes, and direct contact results in corneal opacity (permanent clouding of the eye). GLOVES: Wear impervious rubber gloves to prevent skin contact. RESPIRATOR: Use a NIOSH-approved respirator per the NIOSH *Pocket Guide to Chemical Hazards* (Genium ref. 88) for the maximum-use concentrations and/or the exposure limits cited in section 2. Follow the respirator guidelines in 29 CFR 1910.134. Any detectable concentration of ethylene dichloride requires an SCBA, full facepiece, and pressure-demand/positive-pressure modes. Warning: Air-purifying respirators will not protect workers from oxygen-deficient atmospheres. OTHER: Wear rubber boots, aprons, and other protective clothing suitable for use conditions to prevent skin contact. Remove contaminated clothing and launder it before wearing it again. Discard contaminated shoes. VENTILATION: Provide maximum explosion-proof local fume exhaust ventilation systems to maintain the airborne concentrations of ethylene dichloride vapors below the exposure limits cited in section 2. Install properly designed hoods that maintain a minimum face velocity of 100 lfm (linear feet per minute). SAFETY STATIONS: Make eyewash stations, washing facilities, and safety showers available in areas of use and handling. SPECIAL CONSIDERATIONS: Vapors are heavier than air and will collect in low-lying areas. Eliminate sources of ignition in these areas and again provide good ventilation there. COMMENTS: Practice good personal hygiene. Keep materials off of your clothes and equipment. Avoid transferring this material from hands to mouth while eating, drinking, or smoking. Immediately remove ethylene dichloride-saturated clothing to avoid flammability and health hazards. Contact lenses pose a special hazard; soft lenses may absorb irritants, and all lenses concentrate them.

SECTION 9. SPECIAL PRECAUTIONS AND COMMENTS

STORAGE SEGREGATION: Store ethylene dichloride in tightly closed containers in a cool, dry, well-ventilated area away from sources of ignition. Protect containers from physical damage and from exposure to excessive heat. Avoid direct physical contact with strong acids, bases, oxidizing agents, and reducing agents. SPECIAL HANDLING/STORAGE: Use nonsparking tools. Outside or detached storage is preferred. Store and handle ethylene dichloride in accordance with the regulations concerning OSHA class IB flammable liquids. ENGINEERING CONTROLS: During transfer operations involving ethylene dichloride, the liquid and its vapors must not be exposed to nearby sources of ignition from engineering systems that are not explosion proof. Preplan emergency response procedures.

TRANSPORTATION DATA (per 49 CFR 172.101-2):

DOT Hazard Class: Flammable Liquid

DOT Label: Flammable Liquid

IMO Class: 3.2

DOT Shipping Name: Ethylene Dichloride

DOT ID No. UN 1184

IMO Label: Flammable Liquid, Poison

References: 1-9, 12, 19, 21, 26, 43, 47, 73, 87-102. CK

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Approvals JO. Recroccio

Indust. Hygiene/Safety DW 11-18-87

Medical Review Hedl Goldsmith 11-30-87

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Material Safety Data Sheet

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GENIUM PUBLISHING CORP.

No. 312
TRICHLOROETHYLENE
(Revision E)

Issued: July 1979
Revised: August 1987

SECTION 1. MATERIAL IDENTIFICATION

23

MATERIAL NAME: TRICHLOROETHYLENE

DESCRIPTION (Origin/Uses): Prepared from *sym*-tetrachloroethane by way of eliminating HCl by boiling with lime. Used to manufacture organic chemicals, pharmaceuticals; in degreasing and dry cleaning; and as a solvent for fats, waxes, rubbers, oils, paints, varnishes, ethers, and cellulose esters.

OTHER DESIGNATIONS: Ethylene Trichloride; TCE; Trichloroethene; 1,1,2-Trichloroethylene; C_2HCl_3; NIOSH *RTECS* #KX4550000; CAS #0079-01-6

MANUFACTURER/SUPPLIER: Available from several suppliers, including: Dow Chemical USA, 2020 Dow Center, Midland, MI 48640; Telephone: (517) 636-1000; (800) 258-CHEM

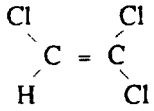
COMMENTS: Trichloroethylene is a toxic solvent and a suspected occupational carcinogen.

HMIS			
H	2	R	1
F	1	I	3
R	1	S	1
PPE*		K	0

* See sect. 8

SECTION 2. INGREDIENTS AND HAZARDS

	%	HAZARD DATA
Trichloroethylene, CAS #0079-01-6; NIOSH *RTECS* #KX4550000	100	ACGIH Values 1987-88 TLV-TWA*: 50 ppm, 270 mg/m^3 TLV-STEL**: 200 ppm, 1080 mg/m^3 OSHA PEL 1986*** 8-Hr TWA: 100 ppm Ceiling: 200 ppm NIOSH REL 1986 10-Hr TWA: 25 ppm TOXICITY DATA Human, Oral, LD_{Lo}: 7 g/kg Human, Inhalation, TC_{Lo}: 6900 mg/m^3 (10 Min) Human, Inhalation, TC_{Lo}: 160 ppm/83 Min Human, Inhalation, TD_{Lo}: 812 mg/kg



* The TLV-TWA is set to control subjective complaints such as headache, fatigue, and irritability.

** The TLV-STEL is set to prevent incoordination and other beginning anesthetic effects from TCE. These levels should provide a wide margin of safety in preventing liver injury.

*** The OSHA PEL is 300 ppm for 5 minutes in any 2 hours.

SECTION 3. PHYSICAL DATA

Boiling Point ... 188.6°F (87°C)
Vapor Pressure ... 58 Torr at 68°F (20°C)
Water Solubility ... Insoluble
Vapor Density (Air = 1) ... 4.53
Evaporation Rate ... Not Listed
Specific Gravity ... 1.4649 at 68°F (20°C)
Melting Point ... -120.64°F (-84.8°C)
Molecular Weight ... 131.40 Grams/Mole

Appearance and odor: Colorless, nonflammable mobile liquid; sweetish odor like chloroform.

COMMENTS: TCE is highly soluble in lipids. A high vapor pressure at room temperature provides the potential for TCE vapors to contaminate use areas.

SECTION 4. FIRE AND EXPLOSION DATA

Flash Point and Method	Autoignition Temperature	Flammability Limits in Air	LOWER	UPPER
Not Listed	770°F (410°C)	% by Volume	8%	10.5%

EXTINGUISHING MEDIA: TCE has no flash point in a conventional closed tester at room temperature, but it is moderately flammable at higher temperatures. Use dry chemical, carbon dioxide, alcohol foam, or other extinguishing agents suitable for the surrounding fire.

OSHA Flammability Class (29 CFR 1910.106): Not Regulated

UNUSUAL FIRE/EXPLOSION HAZARDS: During fire conditions TCE emits highly toxic and irritating fumes, including hydrochloric acid and phosgene. SPECIAL FIRE-FIGHTING PROCEDURES: Wear a self-contained breathing apparatus with a full facepiece operated in a pressure-demand or another positive-pressure mode. At TCE vapor levels of 300-1000 ppm, fire fighters who lack the proper respiratory equipment may experience incoordination and impaired judgment.

DOT Flammability Class (49 CFR 173.115): Not Regulated

SECTION 5. REACTIVITY DATA

Trichloroethylene is stable. Hazardous polymerization can occur under certain circumstances (see Conditions to Avoid and Comments, below).

CHEMICAL INCOMPATIBILITIES include magnesium or aluminum powder, NaOH, KOH, or other strong alkaline materials. Reactions with alkaline materials may lead to the formation of dangerous explosive mixtures of chloroacetylenes.

CONDITIONS TO AVOID: When TCE is heated (as in the case with vapor degreasers) or exposed to sunlight, it requires extra stabilization against oxidation, degradation, and polymerization. It is slowly decomposed by light when moist.

PRODUCTS OF HAZARDOUS DECOMPOSITION include hydrochloric acid and phosgene under certain conditions at elevated temperatures.

COMMENTS: TCE is stable under normal handling and storage conditions, and hazardous polymerization is not expected to occur. However, failure of the stabilizer at elevated temperatures or other extreme conditions may allow polymerization to take place..

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SECTION 6. HEALTH HAZARD INFORMATION

Trichloroethylene is listed as a carcinogen by the NTP, IARC, and OSHA. NIOSH recommends that trichloroethylene be treated as an occupational carcinogen. IARC carcinogenic results are animal suspect, animal positive, and human indefinite. SUMMARY OF RISKS: Moderate exposures to TCE cause symptoms similar to those of alcohol inebriation. Higher concentrations cause narcotic effects. Ventricular fibrillation has been cited as the cause of death following heavy exposures. TCE-induced hepato cellular carcinomas have been detected in mice during tests conducted by the National Cancer Institute (*Chem & Eng News* 54 [April 5, 1976]:4). Organ systems affected by overexposure to TCE are the central nervous system (euphoria, analgesia, anesthesia), degeneration of the liver and kidneys, the lungs (tachypnea), heart (arrhythmia) and skin (irritation, vesication, and paralysis of fingers when immersed in liquid TCE). Contact with the liquid defats the skin, causing topical dermatitis. Certain people appear to experience synergistic effects from TCE exposure concomitant with exposure to caffeine, alcohol, and other drugs. When combined with alcohol intake, toxic effects are increased and may cause a red, blotchy facial and upper body rash commonly called "degreaser's flush." Other reported symptoms of TCE exposure include abnormal fatigue, headache, irritability, gastric disturbances, and intolerance to alcohol. Toxic effects from testing of TCE on humans include hallucination, distorted perception, somnolence (general depressed activity), and jaundice. TARGET ORGANS: Respiratory system, central nervous system, heart, liver, kidneys, and skin. PRIMARY ENTRY: Ingestion, inhalation, skin contact. ACUTE EFFECTS: Headache, vertigo, visual disturbance, tremors, nausea, vomiting, dermatitis, dizziness, drowsiness, and irritation to the eyes, nose, and throat. CHRONIC EFFECTS: None Reported. MEDICAL CONDITIONS AGGRAVATED BY LONG-TERM EXPOSURE: Diseases of the liver, kidneys, lungs, and central nervous system. FIRST AID: EYE CONTACT: Immediately flush eyes, including under the eyelids, gently but thoroughly with plenty of running water for at least 15 minutes. Get medical help.* SKIN CONTACT: Wash thoroughly with soap and water. Remove and launder contaminated clothing before wearing it again; clean material from shoes and equipment. Get medical help.* INHALATION: Remove victim to fresh air; restore and/or support his breathing as needed. Do not give adrenalin to the victim. Get medical help.* INGESTION: Call a poison control center. Never give anything by mouth to someone who is unconscious or convulsing. A professional decision regarding whether or not to induce vomiting is required. Do not give adrenalin to the victim. Get medical help.*

*GET MEDICAL ASSISTANCE = IN PLANT, PARAMEDIC, COMMUNITY. Get prompt medical assistance for further treatment, observation, and support after first aid.

COMMENTS: Workers' responses to TCE vary significantly because of many factors, including age, health status, nutrition, and intake of alcohol, caffeine, and medicines. Do not use these substances before, during, or after exposure to TCE. If a worker displays any of the symptoms of exposure to TCE, thoroughly investigate all the possible contributing factors to determine, if possible, how much the work environment levels of TCE are responsible.

SECTION 7. SPILL, LEAK, AND DISPOSAL PROCEDURES

SPILL/LEAK: Inform safety personnel of any trichloroethylene spill or leak and evacuate the area for large spills. Cleanup personnel must use respiratory and liquid contact protection. Adequate ventilation must be provided. Confine the spilled TCE to as small an area as possible. Do not allow it to run off to sewers or open waterways. Pick up spilled TCE with a vacuum cleaner or an absorbent such as vermiculite.

DISPOSAL: Consider reclamation, recycling, or destruction rather than disposal in a landfill.

Trichloroethylene is designated as a hazardous substance by the EPA (40 CFR 116.4).

Trichloroethylene is reported in the 1983 EPA TSCA Inventory.

EPA Hazardous Waste Number (40 CFR 261.33): U228

EPA Reportable Quantity (40 CFR 117.3): 1000 lbs (454 kgs)

Aquatic Toxicity Rating, TLm 96: Not Listed

SECTION 8. SPECIAL PROTECTION INFORMATION

GOGGLES: Always wear protective eyeglasses or chemical safety goggles. Follow the eye and face protection guidelines of 29 CFR 1910.133. GLOVES: Wear impervious gloves. RESPIRATOR: Use a NIOSH-approved respirator per the *NIOSH Guide to Chemical Hazards* (Genium ref. 88) for the maximum-use concentrations and/or the exposure limits cited in section 2. Follow the respirator guidelines in 29 CFR 1910.134. Any detectable concentration of TCE requires an SCBA, full facepiece, and pressure-demand/positive-pressure modes. WARNING: Air-purifying respirators will not protect workers from oxygen-deficient atmospheres. OTHER EQUIPMENT: Wear rubber boots, aprons, and other suitable body protection appropriate to the existing work environment. VENTILATION: Install and operate general and local exhaust ventilation systems of sufficient power to maintain airborne concentrations of TCE below the OSHA PEL standards cited in section 2. SAFETY STATIONS: Make eyewash stations, washing facilities, and safety showers available in areas of use and handling. Contact lenses pose a special hazard; soft lenses may absorb irritants, and all lenses concentrate them. OTHER SPECIAL MODIFICATIONS IN THE WORKPLACE: Because of the unresolved controversy about the carcinogenic status of TCE, all existing personal protective equipment and engineering technology should be used to prevent any possibility of worker contact with this material.

COMMENTS: Practice good personal hygiene. Keep material off of your clothes and equipment. Avoid transfer of material from hands to mouth while eating, drinking, or smoking. Adhere to the sanitation requirements of 29 CFR 1910.141 and 29 CFR 1910.142.

SECTION 9. SPECIAL PRECAUTIONS AND COMMENTS

STORAGE SEGREGATION: Prevent TCE from coming into contact with strong caustics such as NaOH; KOH; chemically active metal like Ba, Li, Na, Mg, Ti; and powdered aluminum or magnesium in acidic solutions. SPECIAL HANDLING/STORAGE: Store this material in a cool, dry, well-ventilated area. Avoid elevated temperatures because products of toxic and corrosive decomposition from TCE may form. Monitor the level of any stabilizer component that may be added to the TCE. (Consult the technical data from the supplier to determine the specifics of any added stabilizer.) If applicable, follow the supplier's recommendation concerning proper rotation of stock, shelf-life requirements, and levels of stabilizers.

ENGINEERING CONTROLS IN THE WORKPLACE: Avoid collecting aluminum fines (very small particles) or chips in a TCE vapor degreaser. Monitor TCE stabilizer levels regularly. Only trained personnel should operate vapor degreasers.

TRANSPORTATION DATA (per 49 CFR 172.101-2):

DOT Hazard Class: ORM-A	DOT ID No. UN1710	IMO Class: 6.1
IMO Label: St. Andrew's Cross (X)*	DOT Shipping Name: Trichloroethylene	DOT Label: None

* Harmful - Stow away from foodstuffs (IMO Label, Materials of Class 6.1 Packaging Group III).

References: 1-9, 12, 14, 21, 73, 87-94. PI

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Approvals JO Recupero

Indust. Hygiene/Safety 11-18-87

Medical Review

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Material Safety Data Sheet
MSDS: 24654 - TOLUENE
========== 2/20/92

ıtus: Current Revised: 10/23/90

Formula: C7H8 Part Number:
Specification: NOAA# 4654 Keyword:
Synonyms:
Stock Items:

Manufacturer
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Supplier
DATA FROM CAMEO/NOAA
7600 SAND POINT WAY N.E. Phone: (206) 526-6317
SEATTLE, WA 98115 Emergency:

Physical/Chemical Characteristics

Boiling Point .....:	231.1 F	@ 760 mm Hg
Melting Point .....:	-139 F	
Freezing Point .....:		
Pour Point .....:		
Softening Point .....:		
Specific Gravity .....:	0.867	@ 68 Deg F
Vapor Pressure .....:	23.22	@ 70 Deg F
at Temperature ....:	70 F	
Vapor Density .....:		
Percent Volatiles ....:		
Evaporation Rate .....:		
pH .....:		
Molecular Weight .....:	92.14	
Viscosity .....:		
Solubility in Water ..:		

Odor/Appearance/Other Characteristics:

Fire and Explosion Data

Closed Cup Flash Pt. .:	40 F
Open Cup Flash Point .:	
Fire Point .....:	
Auto Ignition .....:	997 F
Lower Explosion Limit :	1.27
Upper Explosion Limit :	7

Shipping Regulations
UN/NA Number: UN1294
DOT Hazard Class:
Shipping Label: FLAMMABLE LIQUID
Shipping Name:

epared
Preparer's Name & Title:
Preparation Date: 10/01/87

Component(s):
TOLUENE
OSHA Pel:
ACGIH TLV: 100 ppm
STEL: 150 ppm
Percent of Product: CAS No.: 108883

Text Section(s)

Full Chemical Name

TOLUENE
CAS number: 108883

Registry of Toxic Effects of Chemical Substances

XS5250000

Standard Transportation Commodities Code

4909305

List of synonyms for the chemical

BENZENE, METHYL-
\ANTISAL 1A
\CP 25
\METHACIDE
\METHYLBENZENE
\METHYLBENZOL
\PHENYLMETHANE
\TOLUENE
\TOLUOL
\METHANE, PHENYL-
\NCI-C07272
\RCRA WASTE NUMBER U220
\TOLUEEN (DUTCH)
\TOLUEN (CZECH)
\TOLUENE (ACGIH,DOT)
\TOLUOL (DOT)
\TOLUOLO (ITALIAN)
\TOLU-SOL
\UN 1294 (DOT)

DOT label

FLAMMABLE LIQUID

NFPA

NFPA rating for Health Hazard --
2
NFPA rating for Flammability Hazard --
3
NFPA rating for Reactivity Hazard --
0

General description of a chemical

Toluene is a clear colorless liquid with a characteristic aromatic odor. It is used in aviation and automotive fuels, as a solvent for many materials, and to make other chemicals. It has a flash point of 40 deg F. It is lighter than water and insoluble in water. Its vapors are heavier than air. ((C)AAR, 1986)

Fire and Explosion Hazards Information

Fire and explosion hazards --
FLAMMABLE. Flashback along vapor trail may occur. Vapor may explode if ignited in an enclosed area. Vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back. (USCG, 1985)
Fire fighting techniques --
Do not extinguish fire unless flow can be stopped. Use water in flooding quantities as fog. Solid streams of water may spread fire. Cool all affected containers with flooding quantities of water. Apply water from as far a distance as possible. Use foam, carbon dioxide or dry chemical. ((C)AAR, 1986)

Protective clothing recommendations

Avoid breathing vapors. Keep upwind. Wear boots, protective gloves, and goggles. Do not handle broken packages without protective equipment. Wash away any material which may have contacted the body with copious amounts of water or soap and water. ((C)AAR, 1986)

Compatibility

Compatibility with Butyl Rubber --
Poor Resistance/Good Data.
Compatibility with chlorinated polyehtylene --
Poor Resistance/Limited Data.
Compatibility with nitrile/butadiene coated fabric --
Good Resistance/Limited Data.
Compatibility with neoprene --
Poor Resistance/Good Data.
Compatibility with nitrile coated fabric --
Poor Resistance/Good Data.
Compatibility with nitrile/PVC coated fabric --
Poor Resistance/Good Data.
Compatibility with polyethylene --
Poor Resistance/Good Data.
Compatibility with polyurethane --
Good Resistance/Limited Data.
Compatibility with polyvinyl alcohol --
Poor Resistance/Good Data.
Compatibility with polyvinyl chloride --
Poor Resistance/Good Data.
Compatibility with natural rubber --
Poor Resistance/Good Data.
Compatibility with Saranex coated tyvex --
Poor Resistance/Good Data.
Compatibility with styrene/butadiene coated fabric --
Poor Resistance/Good Data.
Compatibility with Viton --
Good Resistance/Limited Data.
Compatibility with florine rubber/chloroprene --
Good Resistance/Limited Data.

Evacuation information

Isolate for 1/2 mile in all directions if tank car or truck is involved in fire. (DOT, 1984)

Non-Fire response information

Keep sparks, flames, and other sources of ignition away. Keep material out of water sources and sewers. Build dikes to contain flow as necessary. Attempt to stop leak if without hazard. Use water spray to knock-down vapors. Land spill: Dig a pit, pond, lagoon, holding area to contain liquid or solid material. Dike surface flow using soil, sand bags, foamed polyurethane, or foamed concrete. Absorb bulk liquid with fly ash, cement powder, sawdust, or commercial sorbents. Apply "universal" gelling agent to immobilize spill. Apply fluorocarbon-water

foam to diminish vapor and fire hazard. Water spill: Use natural barriers or oil spill control booms to limit spill motion. Use surface active agent (e.g. detergent, soaps, alcohols) to compress and thicken spilled material. Inject "universal" gelling agent to solidify encircled spill and increase effectiveness of booms. If dissolved, apply activated carbon at ten times the spilled amount in region of 10 ppm or greater concentration. Remove trapped material with suction hoses. Use mechanical dredges or lifts to remove immobilized masses of pollutants and precipitates. Air spill: Apply water spray or mist to knock down vapors. ((C)AAR, 1986)

Health hazard information

VAPOR: Irritating to eyes, nose and throat. If inhaled, will cause nausea, vomiting, headache, dizziness, difficult breathing, or loss of consciousness. LIQUID: Irritating to skin and eyes. If swallowed, will cause nausea, vomiting or loss of consciousness. (USCG, 1985)

First aid information

If this chemical comes in contact with the eyes, immediately wash the eyes with large amounts of water, occasionally lifting the lower and upper lids. Get medical attention immediately. Contact lenses should not be worn when working with this chemical. If this chemical comes in contact with the skin, promptly wash the contaminated skin with soap and water. If this chemical penetrates through the clothing, promptly remove the clothing and wash the skin with soap and water. Get medical attention promptly. If a person breathes in large amounts of this chemical, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible. If this chemical has been swallowed, get medical attention immediately. (NIOSH, 1987)

Fire and Explosion Data

Flash point of chemical --
40 Deg F c.c. (USCG, 1985)
Lower explosive limit --
1.27 % (USCG, 1985)
Upper explosive limit --
7 % (USCG, 1985)
Auto-ignition temperature --
997 Deg F (USCG, 1985)

Physical / Chemical Characteristics

Melting point --
-139 Deg F (USCG, 1985)
Vapor pressure --
23.22 mm Hg @ 70 Deg F (USCG, 1985)
Specific gravity of vapor form --
Not Applicable. (USCG, 1985)
Specific gravity of liquid form --
0.867 @ 68 Deg F (USCG, 1985)
Boiling point --
231.1 Deg F @ 760 mm Hg (USCG, 1985)
Molecular weight --
92.14 (USCG, 1985)

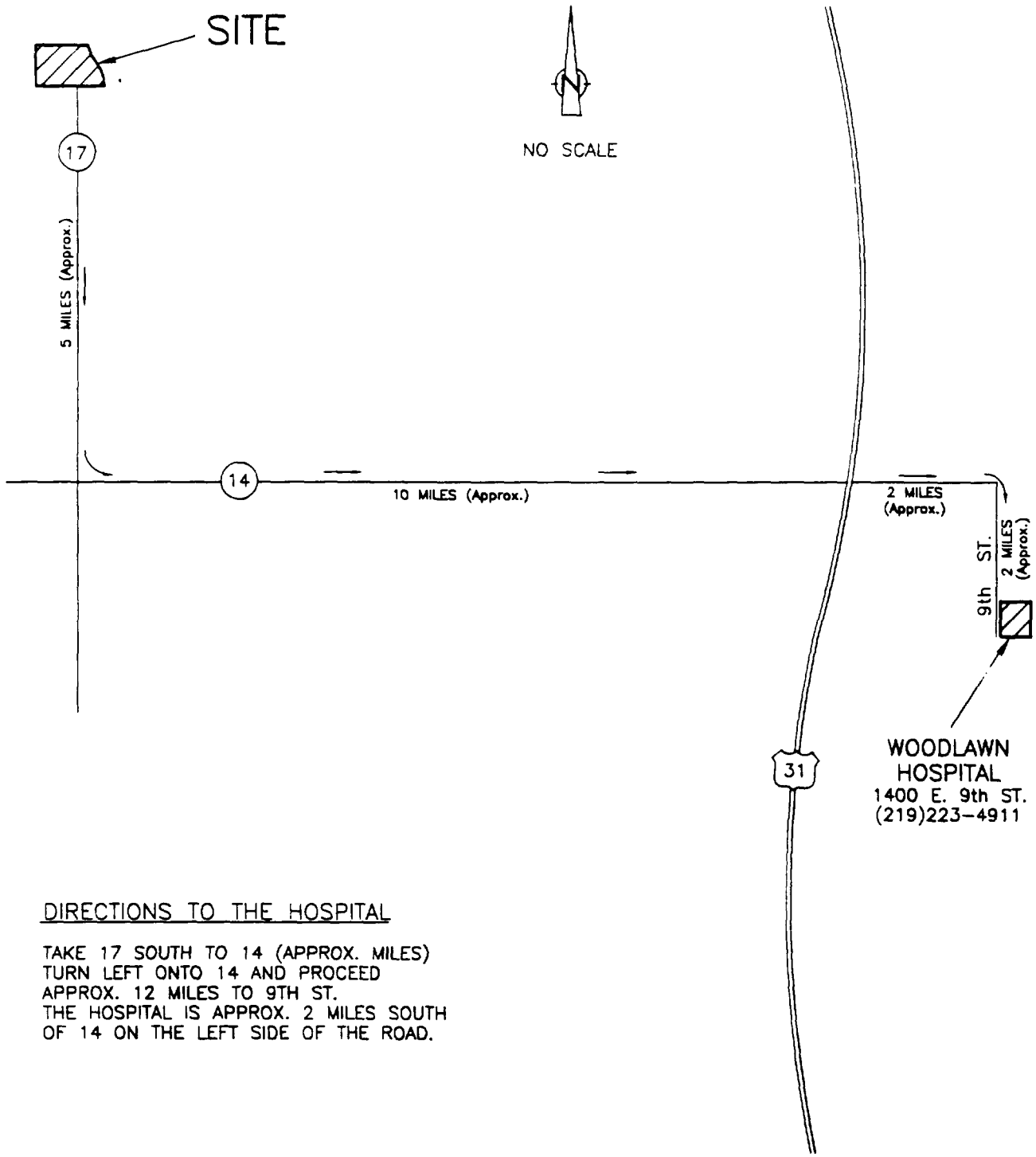
Exposure Limits

NIOSH Immediately Dangerous to Life and Health value --
2000 ppm (NIOSH, 1987)
Time Weighted Average of the Threshold Limit Value --
100 ppm ((C)ACGIH, 1986)
Short Term (15 minute) Exposure limit of the Threshold Limit Value --
150 ppm ((C)ACGIH, 1986)

End of MSDS

ATTACHMENT III

HOSPITAL ROUTE MAP



DIRECTIONS TO THE HOSPITAL

TAKE 17 SOUTH TO 14 (APPROX. MILES)
TURN LEFT ONTO 14 AND PROCEED
APPROX. 12 MILES TO 9TH ST.
THE HOSPITAL IS APPROX. 2 MILES SOUTH
OF 14 ON THE LEFT SIDE OF THE ROAD.

ROUTE TO HOSPITAL
FOUR COUNTY LANDFILL SITE
Fulton County, Indiana

CRA

5369(2)-DEC. 30, 93-REV.0-(C)(M-01)

APPENDIX J

OPERATION AND MAINTENANCE MANUAL

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J.1.0 INTRODUCTION

This manual details the procedures to be used for Site operations and maintenance at the Four County Landfill, in accordance with the Agreed Order entered into between IDEM and the Four County Landfill Group. Personnel responsible for implementing this plan must have completed training and refresher sessions in accordance with 29 CFR 1910.120, and are responsible for being familiar with and performing all work in accordance with the Site Health and Safety Plan.

J.2.0 LEACHATE MANAGEMENT

J.2.1 LEACHATE COLLECTION SYSTEM INSPECTION

A leachate collection system inspection will be performed on each working day. The inspection will include monitoring and recording landfill leachate levels in each of the cells, and inspection of leachate storage areas for leakage or deterioration of containers and dikes.

The daily inspection report will be completed to document the Leachate Collection System Inspection. The daily inspection report form for this purpose is provided in Attachment I. Completed daily inspection reports will be kept in the Site office files. Copies of the reports will be sent to the CRA project oversight manager each week.

J.2.2 LEACHATE COLLECTION, STORAGE, AND TRANSPORT

Leachate is collected by automatic submersible pumps within the primary and secondary leachate system in each cell. The automatic pumps ensure that the leachate level does not exceed one foot above the primary liner. Leachate pumped from the primary and secondary collection systems is temporarily stored in plastic tanks adjacent to each cell. Each working day, leachate is collected from the temporary storage tanks and transported to the central leachate storage area. The volume of leachate pumped from each cell and each system (primary or secondary) will be recorded on the daily inspection report forms.

The collected leachate will be transported to a suitable disposal facility in compliance with federal and state regulations. IDEM will be provided suitable advance notification of any change in the disposal facility accepting the leachate so that a compliance check of the facility may be conducted by IDEM. IDEM will have the authority to approve or disapprove of the disposal facility identified on the basis of the compliance check or other mitigating circumstance.

Each shipment of leachate will be accompanied by an Indiana Uniform Hazardous Waste Manifest. A sample manifest is shown in Attachment II. Manifests will be maintained in on-Site files, and copies will be sent each week to the CRA project oversight manager.

J.2.3 FOCUSED FEASIBILITY STUDY - LEACHATE

The Group is considering performing a focused FS which would evaluate the suitability for disposal of the leachate at a local POTW. The focused FS would evaluate leachate disposal at a POTW with respect to the following criteria:

- Overall protection of human health and environment;
- Compliance with ARARs;
- Long-term effectiveness and permanence;
- Reduction of toxicity, mobility, or volume of materials;
- Short-term effectiveness;
- Implementability;
- Cost;
- USEPA and IDEM acceptance; and
- Community acceptance.

If the group decides to proceed with a focused FS, the completed document would be submitted to IDEM and USEPA.

J.3.0 SURFACE WATER CONTROL

J.3.1 SURFACE WATER COLLECTION AND STORAGE

Surface water runoff at the Site collects in the northeast and southwest settlement ponds, and in the undeveloped portion of Cell C. Surface water that collects in Cell C will be pumped to the northeast settlement pond on an as-needed basis. However, if surface water contained in Cell C appears to have come into contact with leachate, it is not to be transferred and the CRA project oversight manager is to be immediately notified of the situation.

Surface water from the southwest settlement pond will be pumped to the northeast settlement pond on an as-needed basis.

J.3.2 SURFACE WATER DISCHARGES

Surface water discharges are only permitted from the northeast settlement pond and in compliance with the National Pollutant Discharge Elimination System (NPDES) permit for the Four County Landfill. The NPDES permit for the Site is expired; however, the requirements of the permit will be met. All surface water discharges are conducted under controlled conditions. The Site NPDES permit is included in this manual as Attachment III. Personnel responsible for implementing this manual are required to read the NPDES permit. The Site maintenance contractor will be responsible for collecting the required samples of the discharge, delivery of the samples to the project laboratory and provision of required reports, stipulated in the NPDES permit, to IDEM and CRA's project oversight manager.

Discharges from the northeast settlement pond are on an as-needed basis. The discharge from the northeast settlement pond will be recorded on the daily inspection forms. During the discharge, 24-hour composite samples will be collected, and grab samples may also be collected.

Samples will be collected at a point representative of the discharge and prior to entry into the ditch located north of the landfill.

Twenty-four hour composite samples shall consist of at least three individual equal-volume samples taken at equally-spaced time intervals during a 24-hour period, and are combined into one sample for analyses. The following samples will be collected (see also Table J.1):

i) On a weekly basis, a 24-hour composite sample of the discharge will be collected and analyzed for Total Suspended Solids (TSS), and the flowrate in million gallons per day (MGD) will be recorded. A grab sample of the discharge will be collected on a weekly basis and analyzed for pH.

ii) On a monthly basis, a 24-hour composite sample of the discharge will be collected and the sample will be analyzed for Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC).

iii) On a quarterly basis, a 24-hour composite sample of the discharge will be collected and the sample will be analyzed for selected total metals (chromium, copper, cadmium, lead, zinc, nickel, and silver) total phenols, total cyanide, and ammonia. A grab sample will also be collected on a quarterly basis and analyzed for oil and grease and priority pollutant list (PPL) VOC.

iv) On an annual basis, a 24-hour composite sample of the discharge will be collected and analyzed for PPL base/neutral and acid extractable compounds (BNA).

Stormwater discharge monitoring reports (see Attachment IV) will be completed on a monthly basis and submitted to CRA's project oversight manager no later than the 14th day of the month following the monitoring period for review and will be submitted to IDEM no later than the 28th day of the month.

TABLE J.1

NORTHEAST SETTLEMENT POND
NPDES SAMPLING REQUIREMENTS
FOUR COUNTY LANDFILL
FULTON COUNTY, INDIANA

Monitoring Frequency	*Parameters*	*Sample Type*
Weekly	TSS	24-Hr. Composite
Weekly	pH	Grab
Monthly	COD, TOC	24-Hr. Composite
Quarterly	Selected total metals Total cyanide Total phenols Nitrogen (as ammonia)	24-Hr. Composite
Quarterly	Total oil and grease PPL-VOC	Grab
Annually	PPL-BNA	24-Hr. Composite

J.4.0 EQUIPMENT AND BUILDING MAINTENANCE, AND SITE SECURITY

Pumps, hoses, and storage tanks used in the management of leachate and surface water runoff will be maintained. Maintenance activities will include any and all activities necessary to ensure that hoses are in good repair and free from blockages, cracks, or leaks; that storage tanks are not deteriorating or leaking and that valves open and close properly and completely; that pumps achieve correct pressure and flowrate; and that electrical panels are operational and fuses are replaced if needed.

Site buildings which are being used will be maintained. Building windows and doors will be in good working order and capable of being locked securely, or will be repaired so as to prevent unauthorized entry. Buildings will be kept clean. Light bulbs and/or light fixtures will be replaced as necessary to ensure adequate lighting. Utilities will be maintained.

J.5.0 WEEKLY LANDFILL INSPECTION

An overall Site surface inspection will be performed on a weekly basis and after storms. The inspection is to consist of a Site drive along all access roads and perimeter security fence. In areas which are inaccessible by vehicles, the inspection is to be performed by walking the areas. The following is to be noted for the landfill inspection:

1) a determination that fencing and gates are in place;

2) a determination that utilities are operable;

3) an evaluation of the existing landfill cover; and

4) an assessment of the berms and potential for ponding water or washouts.

The weekly inspections performed will be recorded on the weekly inspection report form, included in Attachment IV. Completed forms will be kept in the Site office file. Copies of the completed weekly inspection forms are to be sent to the CRA project manager within 12 hours of the inspection for review and submitted to IDEM within 48 hours.

J.6.0 EROSION CONTROL/CONTROL OF LEACHATE SEEPS

Erosion control and repair of leachate seeps will be performed as required. Activities which may be required to control erosion of leachate seeps include:

- surface soil grading;
- surface soil or rock replacement;
- grass seeding;
- erosion matting of mulch placement;
- soil excavation and recompaction for leachate seep control;
- surface water diversion and control; and
- culvert and drainage pipe repair.

ATTACHMENT I

DAILY INSPECTION FORM

KERAMIDA ENVIRONMENTAL, INC.

FOUR COUNTY LANDFILL

DAILY INSPECTION REPORT

Inspector:_____ Date:_____
(please print)

WEATHER

1. Precipitation in the last 24 hours: No or Yes _____inches
2. Temperature:_____°F
3. Wind direction:_____ Speed: _____mph

Comments:_____

_____

_____

_____

MAINTENANCE BUILDING

1. Leachate Holding Tanks:

Yes	No	
___	___	Evidence of deterioration of containment diking?
___	___	Evidence of deterioration of tank integrity?
___	___	Evidence of leakage?

Liquid Levels? Tank 1_____
(tank quantities) Tank 2_____
Tank 3_____

Date: _____

Comments: _____

_____

_____

_____

ACTIVE PORTION OF LANDFILL

1. Cell A:

Yes	No	
___	___	Properly functioning leachate removal/collection system?
___	___	Presence of leachate in cell?
___	___	Liquids in leak detection system?
___	___	Leachate level one foot above the primary liner?
___	___	Collection tanks and accessories functioning?
___	___	Electrical current operational?
___	___	Has routine maintenance been performed on pumps?

Date of last pump maintenance:

Primary Pump - _____

Secondary Pump - _____

___	___	Leachate levels acceptable?

Amounts of leachate removed:

Collection Cell - _____ gallons

Detection Cell - _____ gallons

___	___	Ponded water noted on cap or berm?
___	___	Signs of burrowing animals?
___	___	Signs of deep root penetration?
___	___	Erosion noted on slopes?
___	___	Is vegetation the proper height and dense enough to prevent erosion?

Comments: _____

_____

_____

_____

Date: _____

2. Cell B:

Yes	No	
___	___	Properly functioning leachate removal/collection system?
___	___	Presence of leachate in cell?
___	___	Liquids in leak detection system?
___	___	Leachate level one foot above the primary liner?
___	___	Collection tanks and accessories functioning?
___	___	Electrical current operational?
___	___	Has routine maintenance been performed on pumps?

Date of last pump maintenance:

Primary Pump -_____

Secondary Pump -_____

___	___	Leachate levels acceptable?

Amounts of leachate removed:

Collection Cell - _____gallons

Detection Cell - _____gallons

___	___	Ponded water noted on cap or berm?
___	___	Signs of burrowing animals?
___	___	Signs of deep root penetration?
___	___	Erosion noted on slopes?
___	___	Is vegetation the proper height and dense enough to prevent erosion?

Comments:_____

_____

_____

_____

3. Cell C:

Yes	No	
___	___	Properly functioning leachate removal/collection system?
___	___	Presence of leachate in cell?
___	___	Liquids in leak detection system?
___	___	Leachate level one foot above the primary liner?

___ ___ Collection tanks and accessories functioning?

___ ___ Electrical current operational?

___ ___ Has routine maintenance been performed on pumps?

Date of last pump maintenance:

Primary Pump -_____

Secondary Pump -_____

___ ___ Leachate levels acceptable?

Amounts of leachate removed:

Collection Cell - _____gallons

Detection Cell - _____gallons

___ ___ Ponded water noted on cap or berm?

___ ___ Signs of burrowing animals?

___ ___ Signs of deep root penetration?

___ ___ Erosion noted on slopes?

___ ___ Is vegetation the proper height and dense enough to prevent erosion?

Comments:_____

_____

_____

_____

TRANSPORTATION AND DISPOSAL

F039 Manifested Leachate transported to disposal on this date:_____

No. of gallons of leachate sent to disposal facility:_____

No. of loads of leachate transported:_____

Manifests properly signed: _____

Copy of manifest sent to: _____

Site's record copy properly filed:_____

Inspection:_____ Date:_____

(signature)

ATTACHMENT II

WASTE MANIFEST FORM

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF SOLID AND HAZARDOUS WASTE MANAGEMENT
P.O. Box 7035
Indianapolis, IN 46207-7035

PLEASE PRINT OR TYPE

Form designed for use on elite (12 pitch) typewriter

Form Approved OMB No. 2050-0039 Expires 9-30-

UNIFORM HAZARDOUS WASTE MANIFEST

Generator's US EPA ID No.

Manifest Document No.

2. Page 1 of

Information in the shaded areas is not required by Federal law, but items D, F, H and I are required by State law.

3. Generator's Name and Mailing Address

A. State Manifest Document Number

INA

B. State Generator's ID

4. Generator's Phone ( )

5. Transporter 1 Company Name

6. Use EPA ID Number

C. State Transporter's ID

D. Transporter's Phone

7. Transporter 2 Company Name

8. Use EPA ID Number

E. State Transporter's ID

F. Transporter's Phone

9. Designated Facility Name and Site Address

10. Use EPA ID Number

G. State Facility's ID

H. Facility's Phone

11. US DOT Description (Including Proper Shipping Name, Hazard Class, and ID Number)	12. Containers No.	Type	13. Total Quantity	14. Unit Wt/Vol.	Waste No.

J. Additional Descriptions for Materials Listed Above

K. Handling Codes for Wastes Listed Above

15. Special Handling Instructions and Additional Information

16. GENERATOR'S CERTIFICATION: I hereby declare that the contents of this consignment are fully and accurately described above by proper shipping name and are classified, packed, marked, and labeled, and are in all respects in proper condition for transport by highway according to applicable international and national government regulations.

If I am a large quantity generator, I certify that I have a program in place to reduce the volume and toxicity of waste generated to the degree I have determined to be economically practicable and that I have selected the practicable method of treatment, storage, or disposal currently available to me which minimizes the present and future threat to human health and the environment; OR, if I am a small quantity generator, I have made a good faith effort to minimize my waste generation and select the best waste management method that is available to me and that I can afford.

Printed/Typed Name | Signature | Month | Date Day | Year

17. Transporter 1 Acknowledgement of Receipt of Materials

Printed/Typed Name | Signature | Month | Date Day | Year

18. Transporter 2 Acknowledgement of Receipt of Materials

Printed/Typed Name | Signature | Month | Date Day | Year

19. Discrepancy Indication Space

20. Facility Owner or Operator: Certification of receipt of hazardous materials covered by this manifest except as noted item 19.

Printed/Typed Name | Signature | Month | Day | Year

EPA Form 8700-22

...se of a spill call the Indiana Office of Environmental Respo... 1 317/241 4336 (day or night) and the ...onal Response Center at 800/424-8802 or 202/426-2675.

ATTACHMENT III

NPDES PERMIT

STATE OF INDIANA

INDIANAPOLIS, 46225

DEPARTMENT OF
ENVIRONMENTAL MANAGEMENT

105 South Meridian Street

September 24, 1986

VIA CERTIFIED MAIL

Mr. Douglas M. Johnson
Vice President
Environmental Waste Control, Inc.
1159 Manchester Avenue
Wabash, Indiana 46992

Re: NPDES Permit No. IN 0048097
Four County Landfill
Rochester, Indiana

Dear Mr. Johnson:

Your application for a National Pollutant Discharge Elimination System (NPDES) Permit for authorization to discharge into an unnamed ditch tributary to the Tippecanoe River has been processed in accordance with Sections 402 and 405 of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1251, et seq.), and the Indiana Environmental Management Act as amended (IC 13-7). The enclosed NPDES Permit covers your facility which operates a sanitary landfill for disposal of low level hazardous wastes. All discharges from this facility shall be consistent with the terms and conditions of this permit.

One condition of your permit requires monthly reporting of several effluent parameters. Reporting is to be done on the enclosed discharge monitoring report form. We have included enough forms to establish a supply for approximately four months of reporting. You should duplicate this form as needed for further reporting.

Another condition which needs to be clearly understood concerns violation of the effluent limitations in the permit. Exceeding the limitations constitutes a violation of the permit and may subject the permittee to criminal or civil penalties. (See Part II A.2.) It is therefore urged that your office and treatment operator understand this part of the permit.

It should be noted that several changes have occurred in the permit since it was first public noticed. These changes are itemized on page three (3) of the Briefing Memo for your review.

It should also be noted that any appeal must be filed under procedures outlined in 330 IAC 5-15 and the enclosed Public Notice. The appeal must be initiated by filing with the Commissioner of the Department of Environmental Management a request for an adjudicatory hearing within 15 days of receipt of this letter. Please send a copy of any written appeal to me at the above address.

If you have any questions, please contact Mr. Robert Kelsey at 517/232-8739.

Sincerely,

Jane T. Magee

Jane Magee
Assistant Commissioner
Office of Water Management

RAK/ab
Enclosures
cc: Chief, Permit Section
U.S. EPA, Region V
Fulton County Health Department

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
AUTHORIZATION TO DISCHARGE UNDER THE
NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM

In compliance with the provisions of the Federal Water Pollution Control Act, as amended by P.L. 92-500 and P.L. 95-217 (33 U.S.C. 1251 et seq., the "Act"), and Public Law 100, Acts of 1972, as amended (IC 13-7, et seq., the "Environmental Management Act"), ENVIRONMENTAL WASTE CONTROL, INC., is authorized to discharge from the FOUR COUNTY LANDFILL facility which is a low level hazardous industrial waste landfill that is located in Rochester, Indiana, to receiving waters named an unnamed ditch in accordance with effluent limitations, monitoring requirements, and other conditions set forth in Parts I and II hereof.

The permit shall become effective on the date of signature.

This permit and the authorization to discharge shall expire at midnight September 23, 1991. In order to receive authorization to discharge beyond the date of expiration, the permittee shall submit such information and forms as are required by the Indiana Stream Pollution Control Board no later than 180 days prior to the date of expiration.

Signed this 24th day of September, 1986, for the Indiana Department of Environmental Management.

Jane Magee
Assistant Commissioner
Office of Water Management

Four County Landfill
IND000780544

The first analysis/scan shall be submitted within forty-five (45) days from the (1) effective date of the permit, or (2) the date sufficient volume in the lagoon is obtained so that a representative sample of the runoff can be collected. The permittee shall notify the IDEM ahead of time if they anticipate not being able to meet the requirement due to insufficient volume in the retention lagoon. If there is no discharge from the storm retention lagoon during this period but sufficient volume is contained in the lagoon in order to guarantee representative samples then grab samples may be taken from the lagoon in order to comply with these initial scan requirements.

Any overflow, increase in volume of a discharge, or discharge from a by-pass system caused by precipitation or snowmelt shall not be subject to the limitations set forth in this permit for TSS. This exemption shall be available only if the facility is designed, constructed, and maintained to contain or treat the volume of water which would fall on the areas covered by this permit during a 25-year 24-hour or larger precipitation event (or snowmelt of equivalent volume). The permittee shall have the burden of demonstrating to the Indiana Department of Environmental Management that the prerequisites to an exemption set forth in this paragraph have been met.

a. The pH shall not be less than 6 nor greater than 9. The pH shall be monitored as follows: by a weekly grab sample.

b. The discharge shall not cause excessive foam in the receiving waters. The discharge shall be essentially free of floating and settleable solids.

c. The discharge shall not contain oil or other substances in amounts sufficient to create a visible film or sheen on the receiving waters.

d. Samples taken in compliance with the monitoring requirements above shall be taken at a point representative of the discharge but prior to entry into the unnamed ditch located north of the landfill.

3. MONITORING AND REPORTING

1. Representative Sampling

Samples and measurements taken as required herein shall be representative of the volume and nature of the monitored discharge.

2. Reporting

The permittee shall submit monitoring reports (DMR-1 form) to the Indiana Department of Environmental Management containing results obtained during the previous month and shall be postmarked no later than the 28th day of the month following each completed monitoring period. The first report shall be submitted by the 28th day of the month following the month in which the permit becomes effective.

If there is to occur a substantial period of time during which there will be no discharge from an authorized outfall, then the permittee may submit a written request to the Indiana Department of Environmental Management for relief from reporting requirements. The Indiana Department of Environmental Management may then suspend reporting requirements without public notice or opportunity for public hearing.

The Regional Administrator may request the permittee to submit monitoring reports to the Environmental Protection Agency if it is deemed necessary to assure compliance of the permit.

3. Definitions

a. Daily Average

(1) Weight Basis - The "daily average" discharge means the total discharge by weight during a calendar month divided by the number of days in the month that the production or commercial facility was discharging. Where less than daily sampling is required by this permit, the daily average discharge shall be determined by the summation of the measured daily discharges by weight divided by the number of days during the calendar month when the measurements were made.

(2) Concentration Basis - The "daily average" concentration means the arithmetic average (proportional to flow) of all daily determinations of concentration made during a calendar month. Daily determinations of concentration made using a composite sample shall be the concentration of the composite sample. When grab samples are used, the daily determination of concentration shall be the arithmetic average (weighted by flow value) of all the samples collected during the calendar day.

b. "Daily Maximum" Discharge

(1) Weight Basis - The "daily maximum" discharge means the total discharge by weight during any calendar day.

(2) Concentration Basis - The "daily maximum" concentration means the daily determination of concentration for any calendar day.

c. 24-hour Composite Sample--Consists of at least 3 individual, equal-volume samples of wastewater which are taken at equally spaced time intervals during a 24-hour period and which are combined prior to analyses.

d. Concentration--The weight of any given material present in a unit volume of liquid. Unless otherwise indicated in this permit, concentration values shall be expressed in milligrams per liter (mg/l).

e. The Regional Administrator is defined as the Region V Administrator, U.S. EPA, located at 230 South Dearborn Street, Chicago, Illinois 60604.

f. The "Commissioner" is defined as the Commissioner of the Indiana Department of Environmental Management which is located at the following address: 105 South Meridian Street, Indianapolis, Indiana 46225.

4. Test Procedures

Test procedures for analysis of pollutants shall conform to regulations published pursuant to Section 304(h) of the Act, the most recent edition of "Standard Methods for the Examination of Water and Wastewater," or other methods approved by the Indiana Department of Environmental Management.

5. Recording of Results

For each measurement or sample taken pursuant to the requirements of this permit, the permittee shall record the following information:

a. The exact place, date, and time of sampling;

b. The dates the analyses were performed;

c. The person(s) who performed the analyses;

d. The analytical techniques or methods used; and

e. The results of all required analyses.

6. Additional Monitoring by Permittee

If the permittee monitors any pollutant at the location(s) designated herein more frequently than required by this permit, using approved analytical methods as specified above, the results of such monitoring shall be included in the calculation and reporting of the values required in the Indiana Department of Environmental Management Monthly Monitoring Report. Such increased frequency shall also be indicated.

7. Records Retention

All records and information resulting from the monitoring activities required by this permit, including all records of analyses performed and calibration and maintenance of instrumentation and recording from continuous monitoring instrumentation, shall be retained for a minimum of three (3) years, or longer, if requested by the Regional Administrator or the Indiana Department of Environmental Management.

C. REOPENING CLAUSE

This permit shall be modified, or, alternatively, revoked and reissued, after public notice and opportunity for hearing to establish appropriate effluent limitations for any parameters disclosed by the required monitoring that threaten violation of applicable water quality standards.

This permit may also be reopened if Federal effluent limitations guidelines are promulgated with additional or more stringent limitations, there are substantial changes in the landfill's structure or operation, or any key information upon which this permit is based is found to be incorrect.

D. BEST MANAGEMENT PRACTICES

The following practices are to be employed in order to best assure compliance with this permit:

1. All reasonable attempts shall be made to divert run-on water away from the active portions of the landfill.

2. All reasonable attempts shall be made to revegetate disturbed areas in order to control erosion.

PART II
STANDARD CONDITIONS FOR NPDES PERMITS
FOR INDUSTRIAL FACILITIES

SECTION A. GENERAL CONDITIONS

1. Duty to Comply

The permittee shall comply with all conditions of this permit. Any permit noncompliance constitutes a violation of the Clean Water Act and the Indiana Environmental Management Act and is grounds for enforcement action, for permit termination, revocation and reissuance, or modification, or for denial of a permit renewal application.

2. Penalties for Violations of Permit Conditions

Pursuant to the Indiana Environmental Management Act, any person who violates a permit condition implementing sections 301, 302, 306, 307, 318, or 405 of the Clean Water Act is subject to a civil penalty not to exceed $25,000 per day of such violation. Any person who willfully or negligently violates permit conditions implementing sections 301, 302, 306, 307, or 308 of the Clean Water Act is subject to a fine of not less than $2,500 nor more than $25,000 per day of violation, or by imprisonment for not more than 1 year or both. If the conviction is for a violation committed after a first conviction of such person under this provision, punishment shall be a fine of not more than fifty thousand dollars ($50,000) per day of violation, or by imprisonment for not more than two (2) years, or both.

Except as provided in permit conditions on "Bypassing," Section B, Paragraph 2 and "Upsets," Section B, Paragraph 3, nothing in this permit shall be construed to relieve the permittee from civil or criminal penalties for noncompliance.

3. Duty to Mitigate

The permittee shall take all reasonable steps to minimize or correct any adverse impact on the environment resulting from noncompliance with the permit.

4. Permit Actions

This permit may be modified, revoked and reissued, or terminated for cause, including, but not limited to, the following:

a. Violation of any terms or conditions of this permit;

b. Obtaining this permit by misrepresentation or failure to disclose fully all relevant facts; or

c. A change in any condition that requires either a temporary or permanent reduction or elimination of the authorized discharge.

The filing of (i) a request by the permittee for a permit modification, revocation and reissuance, or termination, or (ii) a notification of planned changes or anticipated noncompliance does not stay any permit condition.

5. Duty to Provide Information

The permittee shall furnish to the Commissioner, within a reasonable time, any information which the Commissioner may request to determine whether cause exists for modifying, revoking and reissuing, or terminating this permit or to determine compliance with this permit. The permittee shall also furnish to the Commissioner, upon request, copies of records required to be kept by this permit.

6. Duty to Reapply

If the permittee wishes to continue an activity regulated by this permit after the expiration date of this permit, the permittee must apply for and obtain a new permit. The application should be submitted at least 180 days before the expiration date of this permit. The Commissioner may grant permission to submit an application less than 180 days in advance but no later than the permit expiration date.

7. Transfers

This permit is nontransferable to any person except after notice to the Commissioner pursuant to Regulation 330 IAC 5-2-5(c). The Commissioner may require modification or revocation and reissuance of the permit to change the name of the permittee and incorporate such other requirements as may be necessary under the Clean Water Act.

8. Toxic Pollutants

Notwithstanding Paragraph A-4, above, if a toxic effluent standard or prohibition (including any schedule of compliance specified in such effluent standard or prohibition) is established under Section 307(a) of the Clean Water Act for a toxic pollutant which is present in the discharge and such standard or prohibition is more stringent than any limitation for such pollutant in this permit, this permit shall be modified or revoked and reissued to conform to the toxic effluent standard or prohibition.

The permittee shall comply with effluent standards or prohibitions established under section 307(a) of the Clean Water Act for toxic pollutants injurious to human health within the time provided in the regulations that establish those standards or prohibitions, even if the permit has not yet been modified to incorporate the requirement.

9. Containment Facilities

When cyanide or cyanogen compounds are used in any of the processes at this facility, the permittee shall provide approved facilities for the containment of any losses of these compounds in accordance with the requirements of Water Pollution Control Board Regulation 330 IAC 1-2.

10. Operator Certification

The permittee shall have the waste treatment facilities under the direct supervision of an operator certified by the Commissioner as required by IC 13-1-6.

11. Oil and Hazardous Substance Liability

Nothing in this permit shall be construed to relieve the permittee from any responsibilities, liabilities, or penalties to which the permittee is or may be subject under Section 311 of the Clean Water Act.

12. Property Rights

The issuance of this permit does not convey any property rights of any sort or any exclusive privileges, nor does it authorize any injury to private property or an invasion of personal rights, nor any infringement of Federal, State, or local laws or regulations.

13. Severability

The provisions of this permit are severable and, if any provision of this permit or the application of any provision of this permit to any circumstance is held invalid, the application of such provision to other circumstances and the remainder of this permit shall not be affected thereby.

14. Inspection and Entry

The permittee shall allow the Commissioner, or an authorized representative, upon the presentation of credentials and other documents as may be required by law, to:

a. Enter upon the permittee's premises where a regulated facility or activity is located or conducted, or where records must be kept under the conditions of this permit;

b. Have access to and copy, at reasonable times, any records that must be kept under the conditions of this permit;

c. Inspect at reasonable times any facilities, equipment (including monitoring and control equipment), practices, or operations regulated or required under this permit; and

d. Sample or monitor at reasonable times, for the purposes of assuring permit compliance or as otherwise authorized by the Clean Water Act, any substances or parameters at any location.

15. Construction Permit

The permittee shall not construct, install, or modify any water pollution control facility without a valid construction permit issued by the Indiana Department of Environmental Management pursuant to 330 IAC 3.1.

SECTION B. MANAGEMENT REQUIREMENTS

1. Proper Operation and Maintenance

The permittee shall at all times maintain in good working order and efficiently operate all facilities and systems for wastewater collection and treatment which are installed or used by the permittee and which are necessary for achieving compliance with the terms and conditions of this permit.

2. Bypass of Treatment Facilities

a. Definitions:

(1) "Bypass" means the intentional diversion of a waste stream from any portion of a treatment facility normally utilized for treatment of the waste stream.

(2) "Severe property damage" means substantial physical damage to property, damage to the treatment facilities which would cause them to become inoperable, or substantial and permanent loss of natural resources which can reasonably be expected to occur in the absence of a bypass. Severe property damage does not mean economic loss caused by delays in production at the permittee's facility.

b. (Prohibition of Bypass) Bypass which causes or is likely to cause applicable effluent limitations to be exceeded is prohibited unless the following three conditions are met:

(1) Bypass is unavoidable to prevent loss of life, personal injury or severe property damage;

(2) There are no feasible alternatives to bypass, such as the use of auxiliary treatment facilities, retention of untreated wastes, or maintenance during normal period of equipment down-time; and

(3) The permittee submits notice of an unanticipated bypass to the Commissioner within 24 hours of becoming aware of the bypass (if this information is provided orally, a written submission must be provided within five days). Where the permittee knows or should have known in advance of the need for a bypass, this prior notification shall be submitted for approval to the Commissioner, if possible, at least ten days before the date of the bypass.

c. An anticipated bypass which meets the three criteria of Paragraph b of this subsection may be allowed under conditions determined to be necessary by the Commissioner to minimize any adverse effects.

3. Upset Conditions

a. Definition: "Upset" means an exceptional incident in which there is unintentional and temporary noncompliance with technology-based permit effluent limitations because of factors beyond the reasonable control of the permittee. An upset does not include noncompliance to the extent caused by operational error, improperly designed treatment facilities, inadequate treatment facilities, lack of preventive maintenance, or careless or improper operation.

b. (Effect of an upset) An upset shall constitute an affirmative defense to an action brought for noncompliance with such technology-based permit effluent limitations if the requirements of Paragraph c of this subsection are met.

c. (Conditions necessary for a demonstration of upset) A permittee who wishes to establish the affirmative defense of upset shall demonstrate, through properly signed, contemporaneous operating logs or other relevant evidence, that:

(1) An upset occurred and the permittee has identified the specific cause(s) of the upset, if possible;

(2) The permitted facility was at the time being operated in compliance with proper operation and maintenance procedures; and

(3) The permittee complied with any remedial measures required under Paragraph A.3 of this Part.

4. Removed Substances

Solids, sludges, filter backwash, or other pollutants removed from or resulting from treatment or control of wastewaters shall be disposed of in a manner such as to prevent any pollutant from such materials from entering navigable waters and to be in compliance with all Indiana statutes and regulations relative to liquid and/or solid waste disposal.

SECTION C. REPORTING REQUIREMENTS

1. Planned Changes in Facility or Discharge

Any anticipated facility expansions, production increases, or process modifications which will result in new, different, or increased discharges of pollutants must be reported by submission of a new NPDES application or, if such changes will not violate the effluent limitations specified in this permit, by advance notice to the permit issuing authority of such changes. Following such notice, the permit may be modified to revise existing pollutant limitations and/or to specify and limit any pollutants not previously limited.

2. Monitoring Reports

Monitoring results shall be reported at the intervals and in the form specified in Part I.B.2.

3. Compliance Schedules

Reports of compliance or noncompliance with interim and final requirements contained in any compliance schedule of this permit shall be submitted no later than 14 days following each schedule date. Any reports of noncompliance shall include the cause of noncompliance, any remedial actions taken, and the probability of meeting the next scheduled requirement.

4. Twenty-Four Hour Reporting

The permittee shall report information on the following types of noncompliance within 24 hours from the time permittee becomes aware of such noncompliance:

a. Any unanticipated bypass which exceeds any effluent limitation in the permit;

b. Violation of a maximum daily discharge limitation for any of the pollutants listed by the Commissioner in the permit to be reported within 24 hours; and

c. Any noncompliance which may pose a significant danger to human health or the environment.

A written submission shall also be provided within 5 days of the time the permittee becomes aware of the circumstances. The written submission shall contain a description of the noncompliance and its cause; the period of noncompliance, including exact dates and times, and if the noncompliance has not been corrected the anticipated time it is expected to continue; and steps taken or planned to reduce and eliminate the noncompliance and prevent its recurrence. The Commissioner may waive the written report on a case-by-case basis if the oral report has been received within 24 hours.

5. Other Noncompliance

The permittee shall report any instance of noncompliance not reported under Paragraph 3 or 4 of this Section at the time the pertinent Discharge Monitoring Report is submitted. The report shall contain the information specified in Paragraph 4 of this Section.

6. Other Information

Where the permittee becomes aware that he failed to submit any relevant facts or submitted incorrect information in a permit application or in any report to the Commissioner, the permittee shall promptly submit such facts or corrected information.

7. Changes in Discharge of Toxic Substances

The permittee shall notify the Commissioner as soon as it knows or has reason to believe:

a. That any activity has occurred or will occur which would result in the discharge of any pollutant identified as toxic, pursuant to Section 307(a) of the Clean Water Act which is not limited in the permit, if that discharge will exceed the highest of the following "notification levels:"

(1) One hundred micrograms per liter (100 ug/l);

(2) Two hundred micrograms per liter (200 ug/l) for acrolein and acrylonitrile; five hundred micrograms per liter (500 ug/l) for 2,4-dinitrophenol and for 2-methyl-4,6-dinitrophenol; and one milligram per liter (1 mg/l) for antimony;

(3) Five (5) times the maximum concentration value reported for that pollutant in the permit application; or

(4) The level established in Part III of the permit by the Commissioner.

b. That it has begun or expects to begin to use or manufacture as an intermediate or final product or byproduct any toxic pollutant which was not reported in the permit application.

8. Signatory Requirements

a. All reports required by the permit and other information requested by the Commissioner shall be signed and certified by a person described below or by a duly authorized representative of that person:

(1) For a corporation: by a principal executive officer of at least the level of vice-president (including a person who is not a vice-president but performs similar policy-making functions for the corporation);

(2) For a partnership or sole proprietorship: by a general partner or the proprietor, respectively; or

(3) For a Federal, State, or local governmental body or an agency or political subdivision thereof: by either a principal executive officer or ranking elected official.

b. A person is a duly authorized representative only if:

(1) The authorization is made in writing by a person described above.

(2) The authorization specifies either an individual or a position having responsibility for the overall operation of the regulated facility or activity, such as the position of plant manager, operator of a well or a well field, superintendent or position of equivalent responsibility. (A duly authorized representative may thus be either a named individual or any individual occupying a named position.); and

(3) The authorization is submitted to the Commissioner.

c. Certification. Any person signing a document under this section shall make the following certification:

"I certify under penalty of law that I have personally examined and am familiar with the information submitted in this document and all attachments and that, based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment."

9. Availability of Reports

Except for data determined to be confidential under Water Pollution Control Board Regulation 330 IAC 5-1.5, all reports prepared in accordance with the terms of this permit shall be available for public inspection at the offices of the Indiana Department of Environmental Management and the Regional Administrator. As required by the Clean Water Act, permit applications, permits, and effluent data shall not be considered confidential.

10. Penalties for Falsification of Reports

The Indiana Environmental Management Act provides that any person who knowingly makes any false statement, representation, or certification in any record or other document submitted or required to be maintained under this permit, including monitoring reports or reports of compliance or noncompliance, shall, upon conviction, be punished by a fine of not more than $10,000 per violation, or by imprisonment for not more than 6 months per violation, or by both.

WPC 14LL/k
9/9/86

Briefing Memo
October 1984

Four County Landfill
Environmental Waste Control, Inc.
R.R. 4, Box 341
Rochester, IN 46975
Permit No. IND048097

Type of Facility

This facility is a hazardous waste landfill. The west side of this facility is the old municipal waste landfill that is now closed since the permittee is no longer accepting municipal waste. The permittee is licensed to handle low level hazardous waste streams which exhibit only toxic characteristics as defined by EPA and some hazardous industrial wastes which are listed wastes in the Federal Register. All disposal is by landfilling. Waste loads that are not acceptable are those with the following characteristics: 1) flammable, 2) radioactive, 3) acidic pH lower than six, 4) explosive, 5) wastes containing free liquids, and 6) reactive wastes. The permittee is currently handling the following wastes:

EPA Hazardous Waste No.	Waste Characteristics	Amount Estimated for Landfilling
D005	Cadmium wastes	400 - Tons/yr
D007	Chromium wastes	100 - Tons/yr
D008	Lead wastes	400 - Tons/yr
F006	Wastewater Treatment electroplating sludges	600 - Tons/yr
K061	Emission control dust/sludge from primary production of steel in electric furnaces.	20,000 - Tons/yr

This list is not all inclusive since waste disposal approval is granted on a case-by-case basis by the Division of Land Pollution Control.

The facility is located in the NW section of Fulton County covering approximately 61.5 acres. The landfill's capacity is 385,580 yd^3 having an expected life of 17.9 years (10.9 percent completed as of December 1983) and closure is scheduled for the year 2001. The permittee has a RCRA Construction permit where requirements are enforced by the Indiana State Board of Health (permit No. SW-111), which is required for the landfill's construction phase (from initial construction through closure) and the operations of the facility are governed by Operating permit No. OP 25-2 (ISBH). The permittee is pursuing a program to revegetate areas which have been disturbed to minimize soil erosion, and, therefore, the amount of solids discharged.

Water Uses and Treatment

Since all wastes that are accepted by the landfill are wastes

containing free liquids, storm water runoff from the active portions of the landfill will be collected in an earthen basin and will be the only source of wastewater for discharge. Run-on water will be diverted away from the landfill site. The earthen basin (393,000 ft³ capacity with one-foot freeboard) allows settling and flow equalization before the runoff is discharged. The basin shall be designed for a 25-year, 24-hour precipitation event (or snowmelt of equivalent volume). There is currently no point source discharge but the permittee eventually wants to discharge on a controlled continuous basis.

There are two drinking water wells located within one-quarter of a mile from the landfill. The wells are located to the Northeast of the landfill. Groundwater movement in this area is in the northeastern direction.

Receiving Stream

Discharge is to a culvert underneath County Road 525 North, via an unnamed ditch which is located north of the landfill. It is believed that the discharge will flow in a Northeasterly direction, via the culvert, to an underground tile system which will eventually discharge into the Tippecanoe River just north west of the Town of Rochester, Indiana. The discharge is located in the Wabash River Basin. The $Q_{7,10}$ of the ditch is assumed to be 0-cfs and that of the Tippecanoe River just upstream from the point of confluence is approximately 117-cfs (75.6 MGD).

Effluent Limitations Rationale

Surface runoff from landfills, whether for conventional or hazardous waste, does not fall under any promulgated effluent limitations guideline. The proposed permit limits are developed primarily on the basis of Indiana water quality standards, which in all likelihood would be controlling even if there were BCT/BAT guidelines in view of the low flow of the receiving ditch.

The principal contaminants expected in the storm runoff water from the landfill are settleable and suspended solids. The proposed effluent limits for total suspended solids (30 mg/l average and 60 mg/l daily maximum) are designed to meet the minimum qualitative standards in 330 IAC 1-1-6(a) (i.e., State waters shall be free of substances which would be visually unaesthetic or would result in objectionable sediment deposition). The treatment/retention basin to be constructed by the permittee should be capable of attaining these limits.

The permittee does not believe that the storm runoff water from the landfill will contain any pollutants from the hazardous wastes being disposed there. Staff generally agree that as long as the landfill operations are carefully managed, there should be very little contact by stormwater with hazardous waste. At the same time, the very nature of the operation leaves open at least a possibility that storm runoff may be affected by the wastes. Due to this possibility of contamination, the parameters of pH, oil and grease, phenols, and

several toxic metals are limited and to be monitored. Also, toxic organic pollutants are to be monitored only.

More specifically, this proposed permit will require weekly sampling during discharge of total suspended solids (30 mg/l average and 60 mg/l daily maximum) and pH (limited between 6 and 9). Monthly samples for COD and TOC are required and quarterly samples for phenols (4AAP), ammonia (as N), oil and grease, and toxic metals (total chromium, total copper, total cadium, total lead, total zinc, total nickel, total cyanide, and total silver) are required with maximum effluent limitations based on Indiana Water Quality Standards. A quarterly sample is to be analyzed by GC-MS for volatile fraction organics while acid and base/neutral fraction organic compounds are to be analyzed on a yearly basis. These limitations will protect the receiving waters and assure that there is no discharge of toxic materials to the waters of Indiana.

Post Public Notice Addendum - September 1986

As a result of the transfer of authority from the ISPCB to the Indiana Department of Environmental Management on April 1, 1986, all past references to the ISPCB shall now refer to the IDEM and its commissioner. The permit has been changed to reflect this transfer of authority.

Due to the receipt by the IDEM of comments expressing concern about the proposed discharge of storm runoff from the active area(s) of the landfill, staff has decided to require that the first analysis/scan for those indicated pollutants be submitted within 45 days from the effective date of the permit. As a result of this alteration, the first paragraph on page 3 of the permit has been changed to reflect this new requirement.

Expiration Date

A five-year permit is proposed.

Drafted by R. A. Kelsey

BM/Four County BM4

IND

NATIONAL POLLUTANT DISCHARGE
ELIMINATION SYSTEM (NPDES) PERMIT PROGRAM

PUBLIC NOTICE

Issuance of an NPDES Permit to Discharge
into Waters of the State

Indiana Department of Environmental Management
105 South Meridian Street
Indianapolis, IN 46225
317/232-8700

Public Notice Number: SI 6619 RI

Public Notice Issued On: October 1, 1986

Permit No.: IN 0048097

Name and Address of Permittee:

Environmental Waste Control, Inc.
1159 Manchester Avenue
Wabash, Indiana 46992

Name and Address of Facility
Where Discharge Occurs:

Four County Landfill
R.R. 4, Box 341
Rochester, Indiana 46975

I. Permit Information

You are hereby notified that the Assistant Commissioner of the Indiana Department of Environmental Management issued an NPDES permit on September 24, 1986 to the above-named applicant to discharge wastewaters into the Tippecanoe River via an unnamed ditch in FULTON COUNTY, Indiana. The permittee operates a hazardous waste landfill. Landfill operations result in a variable amount per day of stormwater runoff. Parameters to be monitored and/or limited in the discharge include: flow, ammonia (as N), COD, oil and grease, organic compounds, pH, TOC, TSS, and toxic metals, pursuant to applicable State and Federal law. The above-named State waters, into which the discharge is made, are classified for partial-body contact recreation and aquatic life in accordance with State water quality standards.

II. Appeal Procedures

Within fifteen (15) days after the date of publication of this notice, any person aggrieved by the issuance of the above-referenced permit may appeal in writing to the Commissioner of the Indiana Department of Environmental Management for an adjudicatory hearing on the question of whether the permit has been issued in accordance with applicable law.

Such a written request for an adjudicatory hearing must:

(1) state the name and address of the person making the request;
(2) identify the interest of the person making the request;
(3) identify any persons represented by the person making the request;

(4) state with particularity the reasons for the request;
(5) state with particularity the issues proposed for consideration at the hearing; and
(6) identify the permit terms and conditions which, in the judgment of the person making the request, would be appropriate to satisfy the requirements of the law governing permits of the type granted or denied by the Commissioner's action.

Any such request shall be mailed or delivered to:

Nancy A. Maloley, Commissioner
Indiana Department of Environmental Management
105 South Meridian Street
Indianapolis, IN 46225

III. General Information

Copies of the issued NPDES permit, the permit application, and other related documents are on file and may be inspected at the Indiana Department of Environmental Management, Room 636, Chesapeake Building, 105 South Meridian Street, Indianapolis, Indiana, at any time between 9:00 a.m., and 4:00 p.m., Monday through Friday. Copies of this Public Notice and the proposed permit are also available at the Chesapeake Building. These documents may be copied at a cost of 15¢ per page. Please bring the foregoing to the attention of persons whom you know would be interested in this matter.

PN/Four County PN7

INDIANA STREAM POLLUTION CONTROL BOARD MONTHLY MONITORING (DMR-1 Form)
REPORT FOR NPDES DISCHARGE PERMITS

SHEET _____ OF _____

PLEASE COMPLETE AND SUBMIT ONE COPY AT THE END OF EACH MONTH. THIS REPORT MUST READ THE STREAM POLLUTION CONTROL BOARD OFFICE BY THE 28TH OF THE FOLLOWING MONTH

NI			
(1-7) PERMIT NUMBER	(8-10) OUTFALL/ FAC. NO	[illegible] MO	[illegible]

ENTER _____ 1 - INDUSTRY
4 - FEDERAL
(68)

EFFLUENT CHARACTERISTICS		FLOW	pH				
EFFLUENT NO.	(16-21)	0.50050	0.00400	0	0	0	0
SAMPLE TYPE (22-23)	Permit Cond.						
	Monitored						
FREQUENCY (24-28)	Permit Cond						
	Monitored						
EFFLUENT LIMITATIONS	No. Avg. (29-36)						
	Daily Max. (37-44)						

DATE \ UNITS	MGD	HI	LOW	mg/l	lb/day	mg/l	lb/day
1							
2							
3							
4							
5							
6							
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30							
31							
MONTHLY AVERAGE (29-36)							
HIGHEST VALUE OF MONTH (37-44)							
LOWEST VALUE OF MONTH (45-52)							
NO. OF TIMES MAX. EFFLUENT LIMITATIONS EXCEEDED (53-54)							

(SIGNATURE OF CERTIFIED OP

NCIPAL EXECUTIVE OFFICER
ORIZED AGENT)

Four County Landfill
IND000780544

REPORT FOR NPDES DISCHARGE PERMITS

SHEET ____ OF ____

PLEASE COMPLETE AND SUBMIT ONE COPY AT THE END OF EACH MONTH. THIS REPORT MUST REACH THE STREAM POLLUTION CONTROL BOARD OFFICE BY THE 28TH OF THE FOLLOWING MONTH

ENTER ____ 1 - INDUSTRY
4 - FEDERAL

(68)

(1-7) PERMIT NUMBER	(8-10) OUTFALL FAC. NO	(11-12)(13-14) MO YR	

EFFLUENT CHARACTERISTICS									
EFFLUENT NO.	(16-21)	0	0	0	0	0	0	0	0
SAMPLE TYPE (22-23)	Permit Cond.								
	Monitored								
FREQUENCY (24-28)	Permit Cond.								
	Monitored								
EFFLUENT LIMITATIONS	Mo. Ave. (29-36)								
	Daily Max. (37-44)								
DATE	UNITS	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
1									
2									
3									
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31									
MONTHLY AVERAGE	(29-36)								
HIGHEST VALUE OF MONTH	(37-44)								
LOWEST VALUE OF MONTH	(45-52)								
NO. OF TIMES MAX. EFFLUENT LIMITATIONS EXCEEDED	(53-54)								

(SIGNATURE OF CERTIFIED OPERATOR)

(SIGNATURE OF PRINCIPAL EXECUTIVE OFFICER OR AUTHORIZED AGENT)

(PHONE NO.)

Four County Landfill
IND000780544

SUBMITTED (6-66)

NPDES 2 [illegible]

INDIANA STREAM POLLUTION CONTROL BOARD MONTHLY MONITORING (DMR) FORM

REPORT FOR NPDES DISCHARGE PERMITS

SHEET _____ OF _____

PLEASE COMPLETE AND SUBMIT ONE COPY AT THE END OF EACH MONTH. THIS REPORT MUST REACH THE STREAM POLLUTION CONTROL BOARD OFFICE BY THE 28TH OF THE FOLLOWING MONTH.

ENTER 1. INDUSTRY 4. FEDERAL

(1-7) PERMIT NUMBER | (8-10) OUTFALL FAC. NO | (11-12)(13-14) MO YR | (68)

EFFLUENT CHARACTERISTICS		FLOW					
EFFLUENT NO	(15-21)	0 50050	0 00400	0	0	0	0
SAMPLE TYPE (22-23)	Permit Cond						
	Monitored						
FREQUENCY (24-28)	Permit Cond.						
	Monitored						
EFFLUENT LIMITATIONS	Mo. Avg (29-36)						
	Daily Max (37-44)						

DATE	UNITS	MGD		LOW	mg/l	lb/day	mg/l	lb/day
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29								
30								
31								
MONTHLY AVERAGE	(29-36)							
HIGHEST VALUE OF MONTH	(37-44)							
LOWEST VALUE OF MONTH	(45-52)							
NO. OF TIMES MAX EFFLUENT LIMITATIONS EXCEEDED	(53-54)							

(SIGNATURE OF CERTIFIED OPERATOR)

(PRINCIPAL EXECUTIVE OFFICER OR AUTHORIZED AGENT)

Four County Landfill
IND000780544

(PHONE NO.)

(SUBMITTED) (date)

ATTACHMENT IV

WEEKLY INSPECTION FORM

KERAMIDA ENVIRONMENTAL, INC.

FOUR COUNTY LANDFILL

WEEKLY INSPECTION REPORT

Inspector:_____ Date:_____
(please print)

ON-SITE CONDITIONS

1. General Site:

Yes	No	
___	___	Access gate operating properly?
___	___	Warning Signs properly displayed?
___	___	Any signs of unlawful entry?
___	___	Damage to perimeter fencing or gate (i.e., cuts, breaks, undermining by animals, etc.)?
___	___	Are the utilities (electric, water, and natural gas) operational?

Comments:_____

_____

_____

_____

_____

2. Run-off Ponds:

Yes	No	
___	___	Drainage system functioning properly?
___	___	Hoses in good operating conditions?
___	___	Pumps working properly?

Date: _____

___	___	Pond levels acceptable?
___	___	Signs of burrowing animals?
___	___	Are pond banks showing excessive erosional problems?
___	___	Transferred water from SW to the NE settlement pond?
___	___	Discharged water in accordance with the NPDES permit?
___	___	Has a composite water sample been taken during the 24-hour discharge period?
___	___	Has a composite water sample been sent in for laboratory analysis? (If yes, was it acceptable? _____)

Comments: _____

_____

_____

_____

_____

3. Cell A:

Yes	No	
___	___	Water ponding noted on cap or berm?
___	___	Signs of burrowing animals?
___	___	Erosion noted on slopes?
___	___	Leachate breakout noted?
___	___	Is vegetation the proper height and dense enough to prevent erosion?

Comments: _____

_____

_____

_____

_____

Date: _____

4. Cell B:

Yes	No	
___	___	Water ponding noted on cap or berm?
___	___	Signs of burrowing animals?
___	___	Erosion noted on slopes?
___	___	Leachate breakout noted?
___	___	Is vegetation the proper height and dense enough to prevent erosion?

Comments: _____

_____

_____

_____

_____

5. Cell C:

Yes	No	
___	___	Water ponding noted on cap or berm?
___	___	Signs of burrowing animals?
___	___	Erosion noted on slopes?
___	___	Leachate breakout noted?
___	___	Is vegetation the proper height and dense enough to prevent erosion?

Comments: _____

_____

_____

_____

_____