KAR LABORATORIES, INC.

PERFORMANCE EVALUATION STUDIES

KAR Project #
003265
(WP045)

WP Performance Summary

July 2000

APG Customer Code: 1892

Kar Laboratories Inc.

4425 Manchester Road
Kalamazoo, MI 49001

Analytical Products Group, Inc.
2730 Washington Boulevard • Belpre, Ohio 45714 • 800.272.4442 • Fax 740.423.5588

WP Performance Summary Introduction

Introduction:

The APG Proficiency Testing Program has been designed to evaluate your laboratory's performance against other participating laboratories on the same set of standards. Sample levels have been chosen to meet the requirements as specified by the National Standards for Water Proficiency Testing Studies Criteria Document (Document # NERL-Ci-0045) and the NELAP Standards, to assist you in ensuring that the procedure is in-control. In most cases, sample levels are not designed to challenge the detection limits of the method.

The following information is provided to assist you in the interpretation of the report. All statistical measures have been calculated based upon generally accepted formulae.

Your Result:

Every effort has been made to insure correct data entry. Should you find a data entry error, please notify Analytical Products Group and we will adjust the data and reissue the report.

Assigned Value:

The reported Assigned Value is the calculated True Value of the standard based upon the actual composition of the standard.

Certified Value:

Verification of the Assigned Value based upon analysis by APG versus a NIST SRM or an external standard if a NIST SRM is not available. The reported Uncertainty is expressed as 2s/Ön.

EPA Mean:

This value is the Mean value calculated as required by the US EPA National Standards for Water Proficiency Testing Program or is the actual Mean for non-EPA parameters

EPA Standard Deviation:

This parameter is also calculated based upon the National Standards for Water Proficiency Testing Program or is the actual Standard Deviation for non-EPA parameters.

Solids Standards

Solids standards are individually prepared and each standard has a unique Assigned Value. The EPA Mean and Standard Deviation are calculated on

Deviation from the Mean or Z score

This result is an expression of how far your reported value was from the Mean of all reporting laboratories in terms of number of Standard Deviations. As a point of reference, EPA Warning Limits are 2 deviations from the Mean and EPA Acceptance Limits are 3 deviations from the Mean.

Evaluation Line:

Following the Deviation from the Mean for each parameter is an Evaluation line. The Evaluation line may have one of five entries:

'<' Evaluation

We have implemented the '<' reporting and evaluation method as specified in the National Standards for Water Proficiency Testing Criteria Document. This program allows laboratories to have non-detects evaluated as acceptable results if they are properly reported. If your laboratory correctly reports a negative result it will be evaluated as 'Acceptable' if you report a zero (0), or less than (<) value for the parameter. The US EPA Database cannot evaluate any other reported result. Therefore, if you report any other value such as ND, Not Detected, BDL, etc the data will be evaluated as 'Unusable' and you will not receive credit for the result. However, if you report a blank result for a parameter it will not be evaluated in your report. A less than (<) value will only be judged 'Acceptable' for a parameter which is present if the acceptance limit includes zero and the entire range represented by the less than result is included in the acceptance limit.

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Evaluation Line (Cont):

Entry	Description
Unusable	A text value was reported which could not be evaluated
Check for Error	Data between 2 and 3 Deviations from the Mean. Data outside the 95% Confidence Interval but within EPA Acceptance Limits.
Not Acceptable	Data more than 3 Deviations from the Mean. Data outside the 99% Confidence Interval, outside the EPA Acceptance Limits.
Blank	No data was reported for this parameter.
Acceptable	Data within acceptable limits.

These notations can be used as a guideline in evaluating your performance.

Comment Section

This section contains comments submitted to Analytical Products Group by program participants. It also contains comments from APG to participants concerning unusual characteristics of the data set or problems with standards which could influence the interpretation of the data.

Performance Evaluation Summary

This section summarizes performance data in a format similar to the USEPA DMR-QA Report. Detailed information on each parameter is included in the main report.

Certification

This program meets the requirements of the ISO/REMCO Harmonized Protocol for Proficiency Testing of Analytical Laboratories as well as the requirements of ASTM E1301. The statistical techniques used to evaluate the data are consistent with ISO and ASTM guidelines and the National Standards for Water Proficiency Testing Programs. APG is an ISO9001 Certified provider of Proficiency Testing Programs.

Introduction to Laboratory Benchmarking System:

The enclosed report includes a ranking summary of your laboratory's performance in the PT program. Several different measures of performance are provided and each should be interpreted separately. The following sections provide a description of the various ranking methods and their interpretation. These rankings are based upon a broad group of laboratories which analyzed the same samples as your laboratory. Laboratories in the program analyzed the samples as single blind PT samples.

Percent Acceptable Data:

The percent acceptable data is calculated as the percent of actual results reported which were within 99% confidence limits for the parameter. Results are reported for your laboratory and the overall average percent acceptable data achieved by all laboratories.

Rank on Percent Acceptable Data:

This is your laboratory's relative rank out of all possible ranks of in the current study. It should be noted that several laboratories can achieve the same rank. The total number of laboratories reporting data for this study is also reported.

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Average Percentile

The report includes your laboratory's rank on each parameter and the related percentile rank for that parameter. The average percentile is the average of this data across all parameters reported. It is a different measure of performance than percent acceptable data since it is effected by your relative performance on each parameter. The report provides an average for this measure for all laboratories reporting as well as your laboratory's performance.

Weighted Rank on Percent Acceptable

Because the database includes laboratories of many sizes and capabilities, APG has provided a weighted rank based upon percent acceptable. This measure considers the number of parameters which were run by each laboratory and weights the rank by the total number of parameters evaluated.

Weighted Rank on Average Percentile

This measure also considers the number of paramcters run by the laboratory. The weighted rank on percentile data considers not only if the analysis was within the limits but also how close to the Mean the reported result was and the total number of analyses run by the laboratory.

Philip C. Coyner
Proficiency Program Manager

Laboratory Benchmark Report

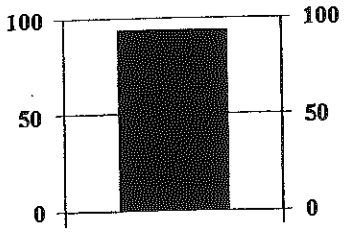
Summary of Ranking Data

Summary of National Ranking Data

Total Number of Laboratories Reporting:	162
Average Percent Acceptable Data:	94.01%
Average Percentile for all Parameters:	61.89%

National Avg % Acceptable

94.0 %

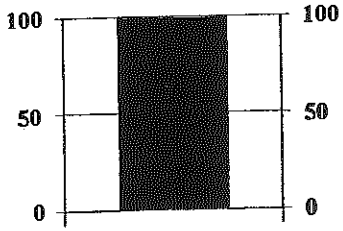


Summary of Laboratory Ranking:

Total Data Points Reported:	287
Number of Acceptable Data Points::	284
Percent Acceptable Data:	98.95%
Average Percentile for all Parameters:	61.82%

Laboratory Avg % Acceptable

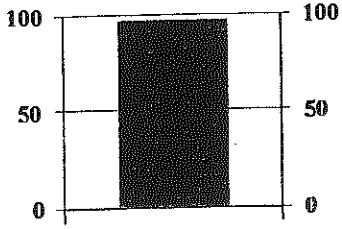
98.95%



Rank on Percent Acceptable Data:	5 of 69
Rank on Average Percentile Data:	94 of 155
Weighted Rank on Percent Acceptable	6 of 89
Weighted Rank on Average Percentile Data:	6 of 159

Weighted Rank Avg Percentile

96.2 %



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Performance Summary

Product: Acid Extractables

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
2,4,6-Trichlorophenol	WP		<5					Acceptable
2,4,6-Trichlorophenol	APG+		<5					Acceptable
2,4-Dichlorophenol	WP		<5					Acceptable
2,4-Dichlorophenol	APG+		<5					Acceptable
2,4-Dimethylphenol	WP		29.496	35	10.1-45.4	0.29		Acceptable
2,4-Dimethylphenol	APG+		100.175	127	17.5-165	0.35		Acceptable
2,4-Dinitrophenol	WP		<5					Acceptable
2,4-Dinitrophenol	APG+		<5					Acceptable
2-Chlorophenol	WP		17.7207	20.4	6.91-24.4	0.73		Acceptable
2-Chlorophenol	APG+		154.026	202	56.7-235	0.27		Acceptable
2-Methyl-4,6-Dinitrophenol	WP		72.9093	51.8	9.92-58.1	4.85		**Not Acceptable**
2-Methyl-4,6-Dinitrophenol	APG+		115.878	142	49.6-140	1.38		Acceptable
2-Nitrophenol	WP		21.16	26.1	6.96-33.1	0.27		Acceptable
2-Nitrophenol	APG+		54.829	60.2	20.2-76	0.72		Acceptable
4-Chloro-3-methylphenol	WP		25.4627	32	10.6-40.3	0.007		Acceptable
4-Chloro-3-methylphenol	APG+		50.772	54	35.1-60.1	0.76		Acceptable
4-Nitrophenol	WP		35.395	80.4	0-104	0.19		Acceptable
4-Nitrophenol	APG+		95.857	160	0-175	0.68		Acceptable
Pentachlorophenol	WP		68.1743	72.5	4.58-98.8	1.05		Acceptable
Pentachlorophenol	APG+		140.66	147	33.4-188	1.15		Acceptable
Phenol	WP		21.5643	42.9	0-55	0.15		Acceptable
Phenol	APG+		42.554	76	0-87.7	0.29		Acceptable

Performance Summary

Study Closing Date 08/16/2000

Product: Base Neutral Extractables

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,2,4-Trichlorobenzene	WP		30.578	49.2	11.1-61.7	0.69		Acceptable
1,2,4-Trichlorobenzene	APG+		80.6793	131	15.9-168	0.44		Acceptable
1,2-Dichlorobenzene	WP	94	61.47	64.6	21.3-76.5	1.37		Acceptable
1,2-Dichlorobenzene	APG+	94	104.596	139	38.9-166	0.11		Acceptable
1,3-Dichlorobenzene	WP		39.925	72	16.6-80.9	0.82		Acceptable
1,3-Dichlorobenzene	APG+		115.78	193	24.9-228	0.3		Acceptable
1,4-Dichlorobenzene	WP		26.693	41.1	10.9-48.6	0.48		Acceptable
1,4-Dichlorobenzene	APG+		90.91	111	18.2-141	0.54		Acceptable
2,4-Dinitrotoluene (2,4-DNT)	WP		<5					Acceptable
2,4-Dinitrotoluene (2,4-DNT)	APG+		<5					Acceptable
2,6-Dinitrotoluene (2,6-DNT)	WP		<5					Acceptable
2,6-Dinitrotoluene (2,6-DNT)	APG+		<5					Acceptable
2-Chloronaphthalene	WP		<5					Acceptable
2-Chloronaphthalene	APG+		<5					Acceptable
3,3'-Dichlorobenzidine	WP		<5					Acceptable
3,3'-Dichlorobenzidine	APG+		<5					Acceptable
4-Bromophenyl phenyl ether	WP		<5					Acceptable
4-Bromophenyl phenyl ether	APG+		<5					Acceptable
4-Chlorophenyl phenyl ether	WP		<5					Acceptable
4-Chlorophenyl phenyl ether	APG+		<5					Acceptable
Acenaphthene	WP		<5					Acceptable
Acenaphthene	APG+		<5					Acceptable
Acenaphthylene	WP		<5					Acceptable

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Acenaphthylene	APG+	<5				Acceptable
Anthracene	WP	20.903	25.5	8.4-37.8	0.45	Acceptable
Anthracene	APG+	51.619	56.9	24.3-72.7	0.39	Acceptable
Benzidine	WP	<5				Acceptable
Benzidine	APG+	<5				Acceptable
Benzo(a)anthracene	WP	<5				Acceptable
Benzo(a)anthracene	APG+	<5				Acceptable
Benzo(a)pyrene	WP	<5				Acceptable
Benzo(a)pyrene	APG+	<5				Acceptable
Benzo(b)fluoranthene	WP	<5				Acceptable
Benzo(b)fluoranthene	APG+	<5				Acceptable
Benzo(ghi)perylene	WP	<5				Acceptable
Benzo(ghi)perylene	APG+	<5				Acceptable
Benzo(k)fluoranthene	WP	<5				Acceptable
Benzo(k)fluoranthene	APG+	<5				Acceptable
Bis(2-Chloroethoxy)methane	WP	<5				Acceptable
Bis(2-Chloroethoxy)methane	APG+	<5				Acceptable
Bis(2-Chloroethyl)ether	WP	<5				Acceptable
Bis(2-Chloroethyl)ether	APG+	<5				Acceptable
Bis(2-Chloroisopropyl)ether	WP	<5				Acceptable
Bis(2-Chloroisopropyl)ether	APG+	<5				Acceptable
Bis(2-Ethylhexyl)phthalate	WP	38.432	60.1	18.8-81.9	1.14	Acceptable
Bis(2-Ethylhexyl)phthalate	APG+	82.191	130	51-157	1.24	Acceptable
Butyl benzyl phthalate	WP	32.967	42.4	0-72.1	0.11	Acceptable
Butyl benzyl phthalate	APG+	91.48	118	0-200	0.34	Acceptable
Chrysene	WP	<5				Acceptable
Chrysene	APG+	<5				Acceptable

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Di-n-butyl phthalate	WP	<5				Acceptable
Di-n-butyl phthalate	APG+	<5				Acceptable
Di-n-octyl phthalate	WP	<5				Acceptable
Di-n-octyl phthalate	APG+	<5				Acceptable
Dibenzo(a,h)anthracene	WP	<5				Acceptable
Dibenzo(a,h)anthracene	APG+	<5				Acceptable
Diethyl phthalate	WP	25.263	32.8	0-54.2	0.067	Acceptable
Diethyl phthalate	APG+	105.656	222	0-355	0.37	Acceptable
Dimethyl phthalate	WP	26.649	23.7	8.71-32.5	1.53	Acceptable
Dimethyl phthalate	APG+	146.76	148	0-257	0.84	Acceptable
Fluoranthene	WP	37.69	46.3	26.3-54.4	0.58	Acceptable
Fluoranthene	APG+	85.53	92.9	37.6-119	0.54	Acceptable
Fluorene	WP	28.955	32.2	17.1-39.2	0.23	Acceptable
Fluorene	APG+	77.186	83.3	39.4-103	0.58	Acceptable
Hexachlorobenzene	WP	17.471	21	7.96-26.3	0.089	Acceptable
Hexachlorobenzene	APG+	49.815	52	16.1-71.1	0.68	Acceptable
Hexachlorobutadiene	WP	38.495	44.9	6.95-57.7	0.73	Acceptable
Hexachlorobutadiene	APG+	67.714	78	4.76-109	0.62	Acceptable
Hexachlorocyclopentadiene	WP	16.527	31.8	3.36-36.1	0.58	Acceptable
Hexachlorocyclopentadiene	APG+	71.652	96.9	0-137	0.32	Acceptable
Hexachloroethane	WP	28.386	47	11.3-55.8	0.69	Acceptable
Hexachloroethane	APG+	60.62	83.8	19.5-99.7	0.076	Acceptable
Indeno(1,2,3-cd)pyrene	WP	<5				Acceptable
Indeno(1,2,3-cd)pyrene	APG+	<5				Acceptable
Isophorone	WP	30.806	39.5	15.9-52.1	0.53	Acceptable
Isophorone	APG+	119.416	137	46.4-173	0.45	Acceptable
N-nitrosodi-n-propylamine	WP	<5				Acceptable

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N-nitrosodi-n-propylamine	APG+	<5				Acceptable
N-nitrosodimethylamine	WP	<5				Acceptable
N-nitrosodimethylamine	APG+	<5				Acceptable
N-nitrosodiphenylamine	WP	<5				Acceptable
N-nitrosodiphenylamine	APG+	<5				Acceptable
Naphthalene	WP	22.683	35.2	14.2-41	1.1	Acceptable
Naphthalene	APG+	50.618	67.7	25.3-78	0.12	Acceptable
Nitrobenzene (NB)	WP	27.992	28.5	9.56-38.4	0.83	Acceptable
Nitrobenzene (NB)	APG+	95.638	99.7	32.9-127	1.02	Acceptable
Phenanthrene	WP	34.427	46.8	21.1-56	0.7	Acceptable
Phenanthrene	APG+	123.022	142	46.8-185	0.3	Acceptable
Pyrene	WP	19.591	21.6	10.2-29.6	0.096	Acceptable
Pyrene	APG+	63.723	70.5	36.4-89.4	0.093	Acceptable

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Product: BTEX

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Benzene	WP		7.8813	7.58	5.13-9.72	0.6		Acceptable
Benzene	APG+		154.9385	143	95.8-179	1.22		Acceptable
Ethylbenzene	WP		9.8017	9.95	6.72-12.9	0.012		Acceptable
Ethylbenzene	APG+		205.8151	200	122-242	1.18		Acceptable
m-Xylene / p-Xylene	WP		6.3907	6.26	3.99-8.8	0.001		Acceptable
m-Xylene / p-Xylene	APG+		56.5302	53.6	40.4-72.8	0.013		Acceptable
o-Xylene	WP		20.8261	19.9	15.5-24	0.73		Acceptable
o-Xylene	APG+		119.8819	119	108-125	1.03		Acceptable
Toluene	WP		12.6942	12.1	9.09-14.6	0.85		Acceptable
Toluene	APG+		69.5993	66.6	48.2-80.3	0.99		Acceptable
Total Xylenes	WP		27.2168	26.2	19.3-33.2	0.44		Acceptable
Total Xylenes	APG+		176.4121	173	123-221	0.27		Acceptable

Product: Fluoride

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Fluoride	WP	29	1.06475	1.12	0.96-1.28	1.04		Acceptable
Fluoride	APG+	29	12.095	12.5	11-13.8	0.72		Acceptable

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Product: Minerals

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Alkalinity as CaCO3	WP	27	40	39.1	34.1-44.8	0.34		Acceptable
Alkalinity as CaCO3	APG+	27	60	59.7	53.3-66.3	0.098		Acceptable
Calcium	WP	23	13.96	14	12.3-16.2	0.36		Acceptable
Calcium	APG+	23	7.90	8.01	6.82-9.43	0.51		Acceptable
Chloride	WP	28	68.5	68	61.2-74.5	0.27		Acceptable
Chloride	APG+	28	77	76.6	69.2-83.9	0.2		Acceptable
Conductivity	WP	20	356	373	324-378	0.56		Acceptable
Conductivity	APG+	20	523	542	477-559	0.36		Acceptable
Magnesium	WP	24	7.46	7.15	6.19-8.09	1		Acceptable
Magnesium	APG+	24	10.52	10.7	9.32-12.1	0.39		Acceptable
Potassium	WP	26	7.12	7.37	6.12-8.65	0.64		Acceptable
Potassium	APG+	26	20.62	21	18-24.1	0.43		Acceptable
Sodium	WP	25	35.82	36.6	32.8-40.6	0.68		Acceptable
Sodium	APG+	25	63.15	64.6	58.2-70.9	0.67		Acceptable
Sulfate	WP	30	18.1	17.7	13.6-21.3	0.46		Acceptable
Sulfate	APG+	30	59.2	61.1	50.3-70.3	0.33		Acceptable
Total Dissolved Solids	WP	21	84	187	134-236	5.91		**Not Acceptable**
Total Dissolved Solids	APG+	21	134	282	209-351	6.19		**Not Acceptable**
Total Hardness as CaCO3	WP	22	70.5	64.6	57.1-72.6	2.17		**Check for Error**
Total Hardness as CaCO3	APG+	22	66.5	64.2	56.8-72.2	0.8		Acceptable

Reported results were miscalculated.
Actual results are twice these
(168 & 268 mg/L, respectively).
—Michael Jaeger, KAR Laboratories (11/16/00)

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Product: PCB's in Oil

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Aroclor 1016/1242 in Oil Sample 1	WP	99	<5					Acceptable
Aroclor 1016/1242 in Oil Sample 2	WP	99	<5					Acceptable
Aroclor 1254 in Oil Sample 1	WP	100	<5					Acceptable
Aroclor 1254 in Oil Sample 2	WP	100	31.6926	42.3	6.97-61.3	0.27		Acceptable
Aroclor 1260 in Oil Sample 1	WP	101	27.5254	38.4	7-54.2	0.39		Acceptable
Aroclor 1260 in Oil Sample 2	WP	101	<5					Acceptable

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Product: PCB's in Water

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Aroclor 1016/1242 Sample 1	WP	40	9.6935	12	3.11-17.1	0.17		Acceptable
Aroclor 1016/1242 Sample 1	APG+	40	4.0706	5.24	1.73-7.18	0.42		Acceptable
Aroclor 1016/1242 Sample 2	WP	40	<0.1					Acceptable
Aroclor 1232 Sample 1	WP	42	<0.1					Acceptable
Aroclor 1232 Sample 1	APG+	42	<0.1					Acceptable
Aroclor 1232 Sample 2	WP	42	<0.1					Acceptable
Aroclor 1248 Sample 1	WP	44	<0.1					Acceptable
Aroclor 1248 Sample 1	APG+	44	<0.1					Acceptable
Aroclor 1248 Sample 2	WP	44	<0.1					Acceptable
Aroclor 1254 Sample 1	WP	45	<0.1					Acceptable
Aroclor 1254 Sample 1	APG+	45	<0.1					Acceptable
Aroclor 1254 Sample 2	WP	45	<0.1					Acceptable
Aroclor 1260 Sample 1	WP	46	<0.1					Acceptable
Aroclor 1260 Sample 1	APG+	46	<0.1					Acceptable
Aroclor 1260 Sample 2	WP	46	8.1667	8.3	4.8-10.7	0.4		Acceptable

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Product: Pesticides

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
4,4'-DDD	WP	49	0.2294	0.21	0.088-0.31	0.78		Acceptable
4,4'-DDD	APG+	49	18.5039	19	9.41-26.5	0.2		Acceptable
4,4'-DDE	WP	50	0.3888	0.4	0.18-0.54	0.48		Acceptable
4,4'-DDE	APG+	50	5.6583	6.11	2.91-8.34	0.039		Acceptable
4,4'-DDT	WP	51	0.4508	0.54	0.23-0.75	0.44		Acceptable
4,4'-DDT	APG+	51	14.4765	14.1	6.51-19.1	0.8		Acceptable
Aldrin	WP	47	0.3957	0.48	0.12-0.65	0.067		Acceptable
Aldrin	APG+	47	5.5656	6.79	1.74-9.17	0.088		Acceptable
alpha-BHC	WP		<0.01					Acceptable
alpha-BHC	APG+		<0.01					Acceptable
beta-BHC	WP		<0.01					Acceptable
beta-BHC	APG+		<0.01					Acceptable
delta-BHC	WP		<0.01					Acceptable
delta-BHC	APG+		<0.01					Acceptable
Dieldrin	WP	48	0.2837	0.27	0.14-0.38	0.59		Acceptable
Dieldrin	APG+	48	7.9246	8.27	4.27-11.4	0.074		Acceptable
Endosulfan I	WP		<0.01					Acceptable
Endosulfan I	APG+		<0.01					Acceptable
Endosulfan II	WP		0.3697	0.36	0.22-0.42	1.47		Acceptable
Endosulfan II	APG+		11.3003	11.4	4.95-15.1	0.77		Acceptable
Endosulfan sulfate	WP		<0.01					Acceptable
Endosulfan sulfate	APG+		<0.01					Acceptable
Endrin	WP		<0.01					

APG Customer 1892 Kar Laboratories Inc.
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Kalamazoo, MI 49001

Performance Summary

WP July 2000
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Endrin	APG+		<0.01				Acceptable
Endrin aldehyde	WP		<0.01				Acceptable
Endrin aldehyde	APG+		<0.01				Acceptable
gamma-BHC	WP		0.1438	0.16	0.065-0.19	0.67	Acceptable
gamma-BHC	APG+		10.9282	12	8.18-12.7	0.7	Acceptable
Heptachlor	WP	52	0.3499	0.4	0.11-0.56	0.27	Acceptable
Heptachlor	APG+	52	18.7306	20.9	5.47-29.2	0.35	Acceptable
Heptachlor epoxide	WP	78	0.1348	0.14	0.067-0.18	0.79	Acceptable
Heptachlor epoxide	APG+	78	14.3762	14.8	7.56-19	0.56	Acceptable
Methoxychlor	WP		0.2384	0.21	0.087-0.32	0.97	Acceptable
Methoxychlor	APG+		13.8675	13.6	9.16-16.4	0.88	Acceptable

APG Customer 1892 Kar Laboratories Inc.
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Performance Summary

Study Closing Date 08/16/2000

Product: Polynuclear Aromatic Hydrocarbons

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Acenaphthene	WP		27.651	31.6	6.75-42.1	0.55		Acceptable
Acenaphthylene	WP		<5					Acceptable
Anthracene	WP		39.385	41.8	16-55.7	0.54		Acceptable
Benzo(a)anthracene	WP		<5					Acceptable
Benzo(a)pyrene	WP		<5					Acceptable
Benzo(b)fluoranthene	WP		<5					Acceptable
Benzo(ghi)perylene	WP		<5					Acceptable
Benzo(k)fluoranthene	WP		<5					Acceptable
Chrysene	WP		<5					Acceptable
Dibenzo(a,h)anthracene	WP		<5					Acceptable
Fluoranthene	WP		20.336	22.4	12.1-26.3	0.48		Acceptable
Fluorene	WP		37.672	40.6	10.2-54.1	0.76		Acceptable
Indeno(1,2,3-cd)pyrene	WP		<5					Acceptable
Naphthalene	WP		35.829	44.5	9-54	0.58		Acceptable
Phenanthrene	WP		26.731	34.4	10.8-43.1	0.05		Acceptable
Pyrene	WP		37.504	45.7	16.2-61.2	0.16		Acceptable

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Kalamazoo, MI 49001

Performance Summary

Study Closing Date 08/16/2000

Product: Polynuclear Aromatic Hydrocarbons-PAH

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Acenaphthene	APG+		58.625	63.5	22.3-88.8	0.27		Acceptable
Acenaphthylene	APG+		<5					Acceptable
Anthracene	APG+		59.568	69.7	16.5-120	0.51		Acceptable
Benzo(a)anthracene	APG+		<5					Acceptable
Benzo(a)pyrene	APG+		<5					Acceptable
Benzo(b)fluoranthene	APG+		<5					Acceptable
Benzo(ghi)perylene	APG+		<5					Acceptable
Benzo(k)fluoranthene	APG+		<5					Acceptable
Chrysene	APG+		<5					Acceptable
Dibenzo(a,h)anthracene	APG+		<5					Acceptable
Fluoranthene	APG+		50.836	50.9	27.9-69.1	0.34		Acceptable
Fluorene	APG+		81.63	85.7	33.9-127	0.06		Acceptable
Indeno(1,2,3-cd)pyrene	APG+		<5					Acceptable
Naphthalene	APG+		63.306	76.9	28.5-99	0.034		Acceptable
Phenanthrene	APG+		91.382	103	39-142	0.051		Acceptable
Pyrene	APG+		86.654	111	36.5-164	0.63		Acceptable

Product: TPH Diesel (DRO)

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
TPH Diesel (DRO)	WP		2.82334	3.02	0-5.16	0.58		Acceptable
TPH Diesel (DRO)	APG+		1.7444	2.01	0-3.36	0.6		Acceptable

APG Customer 1892
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Kar Laboratories Inc.
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Performance Summary

Study Closing Date 08/16/2000

Product: TPH Gasoline (GRO)

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
TPH Gasoline (GRO)	WP		2.012	2.21	0.14-3.84	0.036		Acceptable
TPH Gasoline (GRO)	APG+		2.667	3.06	0.53-4.64	0.13		Acceptable

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Performance Summary

Product: Volatiles

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,1,1-Trichloroethane	WP	56	31.0199	28.2	18.4-37.2	1.03		Acceptable
1,1,1-Trichloroethane	APG+	56	189.3938	187	119-247	0.3		Acceptable
1,1,2,2-Tetrachloroethane	WP		<1					Acceptable
1,1,2,2-Tetrachloroethane	APG+		<1					Acceptable
1,1,2-Trichloroethane	WP		34.2311	32.1	23-38.7	1.28		Acceptable
1,1,2-Trichloroethane	APG+		188.9341	176	115-220	1.2		Acceptable
1,1-Dichloroethane	WP		<1					Acceptable
1,1-Dichloroethane	APG+		<1					Acceptable
1,1-Dichloroethene	WP		16.3626	12.5	6.48-19.8	1.47		Acceptable
1,1-Dichloroethene	APG+		94.9550	80.3	49-125	0.62		Acceptable
1,2-Dichlorobenzene	WP	94	10.1043	9.61	6.41-12.8	0.46		Acceptable
1,2-Dichlorobenzene	APG+	94	64.9907	62.3	44.1-78.5	0.65		Acceptable
1,2-Dichloroethane	WP	54	19.1166	17.4	12.2-23.7	0.64		Acceptable
1,2-Dichloroethane	APG+	54	162.6766	151	104-199	0.69		Acceptable
1,2-Dichloropropane	WP		8.6366	8.16	5.25-10.9	0.6		Acceptable
1,2-Dichloropropane	APG+		126.9083	127	86.5-164	0.15		Acceptable
1,3-Dichlorobenzene	WP	96	11.4482	12	8.21-15.5	0.29		Acceptable
1,3-Dichlorobenzene	APG+	96	103.6579	101	71.9-125	0.58		Acceptable
1,4-Dichlorobenzene	WP	95	15.5367	16.3	11-21.4	0.38		Acceptable
1,4-Dichlorobenzene	APG+	95	78.394	75.1	51.8-96.5	0.57		Acceptable
Benzene	WP	65	18.1212	16.6	11.6-21.8	0.84		Acceptable
Benzene	APG+	65	79.6108	71.4	51.6-91.6	1.2		Acceptable
Bromodichloromethane	WP	60	10.0576	9.18	6.23-12.2	0.86		Acceptable

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Kalamazoo, MI 49001

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Bromodichloromethane	APG+	60	81.3647	76.5	54.4-99.5	0.59	Acceptable
Bromoform	WP	62	42.5665	39.8	25.6-54.6	0.51	Acceptable
Bromoform	APG+	62	114.899	107	70.8-146	0.53	Acceptable
Carbon tetrachloride	WP	58	12.0538	10.9	7.03-15.5	0.61	Acceptable
Carbon tetrachloride	APG+	58	61.8622	53.8	33.2-75.9	1.03	Acceptable
Chlorobenzene	WP	64	27.7123	26.3	18.9-33.3	0.67	Acceptable
Chlorobenzene	APG+	64	128.2946	125	87.1-160	0.41	Acceptable
Chloroform	WP	55	27.1103	23.3	16.4-30.1	1.67	Acceptable
Chloroform	APG+	55	127.1166	120	82.5-153	0.8	Acceptable
cis-1,3-Dichloropropene	WP		<1				Acceptable
cis-1,3-Dichloropropene	APG+		<1				Acceptable
Dibromochloromethane	WP	61	33.4463	30.3	19.1-40.7	0.99	Acceptable
Dibromochloromethane	APG+	61	104.3378	97.4	65.4-127	0.79	Acceptable
Ethylbenzene	WP	66	38.4322	35.1	23.6-45.9	1	Acceptable
Ethylbenzene	APG+	66	139.22	134	88.7-176	0.49	Acceptable
Methylene chloride	WP	63	33.2329	30	19-41.7	0.75	Acceptable
Methylene chloride	APG+	63	113.9205	106	66.8-145	0.63	Acceptable
Tetrachloroethene	WP	59	50.1554	46.6	30.8-59.7	1.01	Acceptable
Tetrachloroethene	APG+	59	160.5351	162	107-206	0.22	Acceptable
Toluene	WP	67	11.4927	10.7	7.36-14	0.72	Acceptable
Toluene	APG+	67	248.2117	240	174-297	0.63	Acceptable
trans-1,2-Dichloroethene	WP		<1				Acceptable
trans-1,2-Dichloroethene	APG+		<1				Acceptable
trans-1,3-Dichloropropene	WP		<1				Acceptable
trans-1,3-Dichloropropene	APG+		<1				Acceptable
Trichloroethene	WP	57	43.0493	40.4	26.3-52.3	0.86	Acceptable
Trichloroethene	APG+	57	88.2876	84.8	54.9-109	0.67	Acceptable

APG

Analytical Products Group, Inc.

PERFORMANCE REPORT

KAR 004218

WS Performance Summary

August 2000

APG Customer Code: 1892

Kar Laboratories Inc.

4425 Manchester Road
Kalamazoo, MI 49001

Laboratory of EXCELLENCE

WS Performance Evaluation Report Introduction and Explanation of Terms

Introduction:
The APG Proficiency Testing Program has been designed to evaluate your laboratory's performance against other participating laboratories on the same set of standards. Sample levels have been chosen to assist you in ensuring that the procedure is in-control. In most cases, sample levels are not designed to challenge the detection limits of the method.

The following information is provided to assist you in the interpretation of the report. All statistical measures have been calculated based upon generally accepted formulae.

Your Result: Every effort has been made to insure correct data entry. Should you find a data entry error please notify Analytical Products Group and we will adjust the data and reissue the report.

Assigned Value: The reported Assigned Value is the calculated True Value of the standard based upon the actual composition of the standard.

Certified Value: Verification of the Assigned Value based upon analysis by APG versus a NIST SRM or an external standard if a NIST SRM is not available. The reported Uncertainty is expressed as $2s/\sqrt{n}$.

EPA Mean: This value is the Mean value calculated as required by the US EPA National Standards for Water Proficiency Testing Program or is the actual Mean for non-EPA parameters

EPA Standard Deviation: This parameter is also calculated based upon the National Standards for Water Proficiency Testing Program or is the actual Standard Deviation for non-EPA parameters

Solids Standards: Solids standards are individually prepared and each standard has a unique Assigned Value. The EPA Mean and Standard Deviation are calculated on the appropriate Assigned Value.

Deviation from the Mean or z score: This result is an expression of how far your reported value was from the Mean of all reporting laboratories in terms of number of Standard Deviations. As a point of reference, EPA Acceptance Limits are 2 deviations from the Mean.

Study Mean: The actual study mean for the analyte. The mean is calculated using all numeric reported values after the removal of outliers, using standard statisitcal methods. The study mean is only reported if a statistically acceptable number of laboratories report numeric results for the analyte.

Study Standard Deviation: The actual standard deviation for the analyte. The standard deviation is calculated using all numeric reported values after the removal of outliers, using standard statistical methods. The study standard deviation is only reported if a statistically acceptable number of laboratories report numeric results for the analyte.

APG
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2730 Washington Boulevard • Belpre, Ohio 45714 • 800.272.44[illegible] [illegible]ax 740.423.5588

Evaluation Line: Determined by the acceptance limits, which are calculated to three significant figures. The Evaluation line may have one of four entries.

Entry	Description
Unusable	A less than or text value was reported which could not be evaluated.
Not Acceptable	Data more than 2 Deviations from the Mean. Data outside the 95% Confidence Interval, outside the EPA Acceptance Limits.
Blank	No data was reported for this analyte or the analyte was not spiked.
Acceptable	Data within acceptable limits.

These notations can be used as a guideline in evaluating your performance.

Comment Section: This section contains comments submitted to Analytical Products Group by program participants. It also contains comments from APG to participants concerning unusual characteristics of the data set or problems with standards which could influence the interpretation of the data.

Performance Evaluation Summary: This section summarizes performance data in a format similar to the USEPA DMR-QA Report. Detailed information on each analyte is included in the main report.

Certification: This program meets the requirements of the ISO/REMCO Harmonized Protocol for Proficiency Testing of Analytical Laboratories as well as the requirements of ASTM E1301. The statistical techniques used to evaluate the data are consistent with ISO and ASTM guidelines and the National Standards for Water Proficiency Testing Programs. APG is an ISO9001 Certified provider of Proficiency Testing Programs.

Sincerely,

Philip C. Coyner
Proficiency Program Manager

Analytical Products Group, Inc.
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APG Customer 1892 Kar Laboratories Inc.
EPA Lab Code MI00041 4425 Manchester Road
Kalamazoo, MI 49001

Performance Summary

WS August 2000
Study Closing Date 09/26/2000

Product: Adipate/Phthalate **Lot Number: 28601**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Bis(2-ethylhexyl) adipate	WS	134	19.088	42	17.6-60.4	1.86		Acceptable
Bis(2-ethylhexyl)phthalate	WS	136	17.887	25.4	10.7-39.5	1		Acceptable

Product: Chlordane (Total) **Lot Number: 28599**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Chlordane	WS	97	7.4943	9.46	5.2-13.7	0.92		Acceptable

Product: Chlorinated Pesticides **Lot Number: 28587**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Aldrin	WS	256	1.166	1.22	0.51-1.53	0.57		Acceptable
Dieldrin	WS	258	1.0797	0.96	0.67-1.2	1.09		Acceptable
Endrin	WS	11	0.407	0.48	0.34-0.63	1.05		Acceptable
Heptachlor	WS	95	0.7165	0.86	0.47-1.25	0.74		Acceptable
Heptachlor epoxide Beta	WS	96	0.3027	0.33	0.18-0.48	0.35		Acceptable
Hexachlorobenzene	WS	172	2.6577	3.08	1.42-3.9	0.002		Acceptable
Hexachlorocyclopentadiene	WS	112	2.2337	3.04	0.12-3.88	0.25		Acceptable
Lindane	WS	12	1.179	1.17	0.64-1.69	0.05		Acceptable
Methoxychlor	WS	13	22.82	28.4	15.6-41.2	0.88		Acceptable
Propachlor	WS	259	1.419	1.5	0.82-2.23	0.29		Acceptable
Trifluralin	WS	244	3.3027	4.52	2.07-6.1	0.78		Acceptable

Performance Summary

Product: EDB/DBCP/TCP **Lot Number: 28584**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,2,3-Trichloropropane	WS		4.16348	3.64	2.18-5.09	0.72		Acceptable
1,2-Dibromo-3-chloropropane	WS	45	0.590375	0.61	0.37-0.86	0.2		Acceptable
Ethylene Dibromide	WS	46	1.385165	1.25	0.75-1.75	0.55		Acceptable

Product: Herbicides **Lot Number: 28597**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
2,4,5-TP (silvex)	WS	16	78.84215	103	51.6-155	0.95		Acceptable
2,4-D	WS	15	81.617225	103	51.6-155	0.84		Acceptable
Acifluorfen	WS	262	18.16832	23.7	5.99-36.3	0.39		Acceptable
Dalapon	WS	115	54.65625	66.6	0-92.9	0.49		Acceptable
Dicamba	WS	247	27.93081	38.3	10.4-53.5	0.37		Acceptable
Dinoseb	WS	116	17.260597	22.5	0.35-33.7	0.027		Acceptable
Pentachlorophenol	WS	102	39.89626	61.1	30.5-91.6	1.39		Acceptable
Picloram	WS	117	33.32519	45.6	0-61.5	0.17		Acceptable

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Performance Summary

WS August 2000
Study Closing Date 09/26/2000

Product: Minerals **Lot Number: 29010-29011**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Alkalinity as CaCO3	WS	27	41.5	41.8	39.7-47	1.01		Acceptable
Calcium	WS		61.60	60.1	56.7-63.8	0.73		Acceptable
Calcium Hardness	WS	25	154	150	141-161	0.56		Acceptable
Chloride	WS		143	142	129-153	0.33		Acceptable
Conductivity	WS		709	728	639-720	1.49		Acceptable
Potassium	WS		72.11	73.5	66.5-80.4	0.4		Acceptable
Sodium	WS	29	19.76	19.2	17.8-21.2	0.34		Acceptable
Sulfate	WS	145	42	41.4	36.9-45.6	0.34		Acceptable
Total Dissolved Solids	WS	24	378	384	274-582	0.65		Acceptable

Product: Nutrients **Lot Number: 28594-28595-28596**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Fluoride	WS	10	5.90	5.88	5.29-6.46	0.082		Acceptable
Nitrate Nitrogen as N	WS	9	5.41	5.22	4.7-5.74	0.73		Acceptable
Nitrite as N	WS	92	1.42	1.43	1.21-1.64	0.073		Acceptable
Orthophosphate as P	WS	261	1.412	1.37	1.29-1.44	1.19		Acceptable

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Kalamazoo, MI 49001

Performance Summary

WS August 2000
Study Closing Date 09/26/2000

Product: Organophosphorus Pesticides **Lot Number: 28598**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Alachlor	WS	93	10.474	12.3	6.76-17.8	0.66		Acceptable
Atrazine	WS	94	3.4355	4.2	2.31-6.09	0.81		Acceptable
Simazine	WS	113	11.764	19.8	4.45-28.3	0.77		Acceptable

Product: PAH **Lot Number: 28600**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Benzo[a]pyrene	WS	122	1.1625	1.5	0.36-1.94	0.041		Acceptable

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EPA Lab Code MI00041 4425 Manchester Road
Kalamazoo, MI 49001

Performance Summary

WS August 2000
Study Closing Date 09/26/2000

Product: Regulated Volatiles **Lot Number: 28585**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,1,1-Trichloroethane	WS	36	20.2445	18.6	14.9-22.3	0.88		Acceptable
1,1,2-Trichloroethane	WS	61	18.5801	17.1	13.7-20.5	0.88		Acceptable
1,1-Dichloroethene	WS	34	20.0591	17.5	14-21	1.45		Acceptable
1,2,4-Trichlorobenzene	WS	76	5.05	6.04	3.62-8.45	0.82		Acceptable
1,2-Dichlorobenzene	WS	54	15.4692	15.1	12.1-18.1	0.24		Acceptable
1,2-Dichloroethane	WS	35	7.4578	6.82	4.09-9.55	0.47		Acceptable
1,2-Dichloropropane	WS	44	16.9478	16.3	13.1-19.6	0.38		Acceptable
1,4-Dichlorobenzene	WS	41	8.8731	9.86	5.92-13.8	0.5		Acceptable
Benzene	WS	39	8.4488	8.13	4.88-11.4	0.2		Acceptable
Carbon tetrachloride	WS	37	5.5234	5.1	3.06-7.14	0.42		Acceptable
Chlorobenzene	WS	49	46.8321	43.4	34.7-52	0.8		Acceptable
cis-1,2-Dichloroethene	WS	43	11.3021	10.3	8.26-12.4	0.95		Acceptable
Dichloromethane	WS	55	15.9002	15.4	12.3-18.5	0.32		Acceptable
Ethylbenzene	WS	48	7.8521	7.77	4.66-10.9	0.053		Acceptable
Styrene	WS	53	15.8038	14.3	11.4-17.1	1.07		Acceptable
Tetrachloroethene	WS	40	12.5365	13.2	10.5-15.8	0.49		Acceptable
Toluene	WS	47	8.3839	8.29	4.97-11.6	0.057		Acceptable
Total Xylenes	WS	90	41.8608	38.8	31.1-46.6	0.78		Acceptable
trans-1,2-Dichloroethene	WS	42	12.3814	11.3	9.03-13.5	0.97		Acceptable
Trichloroethene	WS	38	7.5887	7.51	4.51-10.5	0.053		Acceptable
Vinyl chloride	WS	32	18.1367	18	10.8-25.2	0.038		Acceptable

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Performance Summary

WS August 2000
Study Closing Date 09/26/2000

Product: Residual Chlorine **Lot Number: 28575**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Total Residual Chlorine	WS	22	3.096	1.89	1.54-2.14	8.26		Not Acceptable

Product: Solids **Lot Number: 52676**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Total Dissolved Solids	WS		395	395	380-412	0.12		Acceptable
Total Solids	WS		437	425	405-443	1.37		Acceptable
Total Suspended Solids	WS		25	30.1	18.1-33.5	0.21		Acceptable

Product: Total Cyanide **Lot Number: 28588**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Total Cyanide	WS	146	0.3338	0.4	0.3-0.5	1.32		Acceptable

Product: Total Organic Carbon (TOC) **Lot Number: 28580**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Total Organic Carbon	WS	263	2.9502	2.5	2.18-2.97	1.9		Acceptable

Product: Toxaphene (Total) **Lot Number: 28606**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Toxaphene	WS	14	6.35005	8.4	4.62-12.2	1.08		Acceptable

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Performance Summary

WS August 2000
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Product: Trace Metals **Lot Number: 28590-28591**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Aluminum	WS		394.89	375	310-438	0.65		Acceptable
Antimony	WS	140	28.64	29.5	20.7-38.4	0.2		Acceptable
Arsenic	WS	1	71.74	67.5	59-75.4	1.11		Acceptable
Barium	WS	2	1313.82	1310	1110-1510	0.027		Acceptable
Beryllium	WS	141	3.721	3.74	3.18-4.3	0.068		Acceptable
Boron	WS	226	484.79	436	412-474	2.69		**Not Acceptable**
Cadmium	WS	3	36.79	35.5	28.4-42.6	0.36		Acceptable
Chromium	WS	4	141.34	139	118-160	0.2		Acceptable
Copper	WS	91	1229.88	1220	1100-1340	0.19		Acceptable
Iron	WS		635.77	649	566-713	0.088		Acceptable
Lead	WS	5	87.2	80.5	56.4-105	0.55		Acceptable
Manganese	WS	236	378.78	375	349-395	0.63		Acceptable
Mercury	WS	6	4.552	5.44	3.81-7.08	1.09		Acceptable
Molybdenum	WS	237	132.7	138	117-159	0.48		Acceptable
Nickel	WS	142	393.3	378	322-435	0.53		Acceptable
Selenium	WS	7	85.86	77.2	61.7-92.6	1.12		Acceptable
Silver	WS		106.21	106	95.3-117	0.038		Acceptable
Thallium	WS	143	4.67	4.83	0.8-9.41	0.2		Acceptable
Zinc	WS	239	1993.15	1880	1730-2010	1.76		Acceptable

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Product: Trihalomethanes **Lot Number: 28583**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Bromodichloromethane	WS		10.1595	8.85	5.31-12.4	0.74		Acceptable
Bromoform	WS		46.3493	38.6	30.9-46.3	2.02		**Not Acceptable**
Chloroform	WS		7.9747	7.49	4.49-10.5	0.32		Acceptable
Dibromochloromethane	WS		30.8606	25.8	20.6-31	1.96		Acceptable
Total Trihalomethanes	WS	21	95.3441	80.7	64.6-96.8	1.81		Acceptable

Product: Turbidity **Lot Number: 28576**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Turbidity	WS	23	1.76	1.99	1.7-2.5	1.71		Acceptable

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Performance Summary

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Product: Unregulated Volatiles **Lot Number: 28586**

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,1,1,2-Tetrachloroethane	WS	63	14.1244	12.6	10.1-15.1	1.21		Acceptable
1,1,2,2-Tetrachloroethane	WS	65	10.59	9.93	5.96-13.9	0.33		Acceptable
1,1-Dichloroethane	WS	56	14.5065	14.2	11.3-17	0.24		Acceptable
1,1-Dichloropropene	WS	58	6.7725	7.02	4.21-9.84	0.18		Acceptable
1,2,3-Trichlorobenzene	WS	77	12.1275	14	11.2-16.7	1.31		Acceptable
1,2,3-Trichloropropane	WS	64	11.067	11	8.79-13.2	0.077		Acceptable
1,2,4-Trimethylbenzene	WS	75	<1					Acceptable
1,3,5-Trimethylbenzene	WS	82	<1					Acceptable
1,3-Dichlorobenzene	WS	66	8.7492	8.85	5.31-12.4	0.058		Acceptable
1,3-Dichloropropane	WS	59	18.004	17	13.6-20.3	0.62		Acceptable
2,2-Dichloropropane	WS	60	10.6507	10.1	8.09-12.1	0.53		Acceptable
2-Chlorotoluene	WS	71	15.9775	15.6	12.4-18.7	0.27		Acceptable
4-Chlorotoluene	WS	72	<1					Acceptable
4-Isopropyltoulene	WS	83	<1					Acceptable
Bromobenzene	WS	67	<1					Acceptable
Bromochloromethane	WS	89	<1					Acceptable
Bromodichloromethane	WS	19	<1					Acceptable
Bromoform	WS	18	<1					Acceptable
Bromomethane	WS	69	<1					Acceptable
Chlorodibromomethane	WS	20	9.1125	8.13	4.88-11.4	0.6		Acceptable
Chloroethane	WS	70	<1					Acceptable
Chloroform	WS	17	15.1608	14.9	11.9-17.9	0.18		Acceptable
Chloromethane	WS	68	<1					Acceptable

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cis-1,3-Dichloropropene	WS	152	3.9028	3.7	2.22-5.17	0.28	Acceptable
Dibromomethane	WS	57	11.5028	10.4	8.36-12.5	1.01	Acceptable
Dichlorodifluoromethane	WS	88	<1				Acceptable
Fluorotrichloromethane	WS	87	<1				Acceptable
Hexachlorobutadiene	WS	81	15.1592	14.8	11.8-17.7	0.25	Acceptable
Isopropylbenzene	WS	84	6.7273	7.24	4.34-10.1	0.35	Acceptable
MTBE	WS		40.0442	40	33.6-50.8	0.5	Acceptable
n-Butylbenzene	WS	79	4.2558	4.66	2.8-6.53	0.43	Acceptable
n-Propylbenzene	WS	78	4.6125	5.38	3.23-7.54	0.72	Acceptable
sec-Butylbenzene	WS	86	11.3164	11.2	8.95-13.4	0.12	Acceptable
tert-Butylbenzene	WS	85	17.485	17.8	14.2-21.4	0.17	Acceptable
trans-1,3-Dichloropropene	WS	153	17.284	15.7	12.5-18.8	1.04	Acceptable

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WP Performance Summary

July 2000

APG Customer Code: 1892

Kar Laboratories Inc.

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WP Performance Summary Introduction

Introduction:

The APG Proficiency Testing Program has been designed to evaluate your laboratory's performance against other participating laboratories on the same set of standards. Sample levels have been chosen to meet the requirements as specified by the National Standards for Water Proficiency Testing Studies Criteria Document (Document # NERL-Ci-0045) and the NELAP Standards, to assist you in ensuring that the procedure is in-control. In most cases, sample levels are not designed to challenge the detection limits of the method.

The following information is provided to assist you in the interpretation of the report. All statistical measures have been calculated based upon generally accepted formulae.

Your Result:

Every effort has been made to insure correct data entry. Should you find a data entry error, please notify Analytical Products Group and we will adjust the data and reissue the report.

Assigned Value:

The reported Assigned Value is the calculated True Value of the standard based upon the actual composition of the standard.

Certified Value:

Verification of the Assigned Value based upon analysis by APG versus a NIST SRM or an external standard if a NIST SRM is not available. The reported Uncertainty is expressed as 2s/Ön.

EPA Mean:

This value is the Mean value calculated as required by the US EPA National Standards for Water Proficiency Testing Program or is the actual Mean for non-EPA parameters

EPA Standard Deviation:

This parameter is also calculated based upon the National Standards for Water Proficiency Testing Program or is the actual Standard Deviation for non-EPA parameters.

Solids Standards

Solids standards are individually prepared and each standard has a unique Assigned Value. The EPA Mean and Standard Deviation are calculated on

Deviation from the Mean or Z score

This result is an expression of how far your reported value was from the Mean of all reporting laboratories in terms of number of Standard Deviations. As a point of reference, EPA Warning Limits are 2 deviations from the Mean and EPA Acceptance Limits are 3 deviations from the Mean.

Evaluation Line:

Following the Deviation from the Mean for each parameter is an Evaluation line. The Evaluation line may have one of five entries:

'<' Evaluation

We have implemented the '<' reporting and evaluation method as specified in the National Standards for Water Proficiency Testing Criteria Document. This program allows laboratories to have non-detects evaluated as acceptable results if they are properly reported. If your laboratory correctly reports a negative result it will be evaluated as 'Acceptable' if you report a zero (0), or less than (<) value for the parameter. The US EPA Database cannot evaluate any other reported result. Therefore, if you report any other value such as ND, Not Detected, BDL, etc the data will be evaluated as 'Unusable' and you will not receive credit for the result. However, if you report a blank result for a parameter it will not be evaluated in your report. A less than (<) value will only be judged 'Acceptable' for a parameter which is present if the acceptance limit includes zero and the entire range represented by the less than result is included in the acceptance limit.

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WP Performance Summary Introduction

Evaluation Line (Cont):

Entry	Description
Unusable	A text value was reported which could not be evaluated
Check for Error	Data between 2 and 3 Deviations from the Mean. Data outside the 95% Confidence Interval but within EPA Acceptance Limits.
Not Acceptable	Data more than 3 Deviations from the Mean. Data outside the 99% Confidence Interval, outside the EPA Acceptance Limits.
Blank	No data was reported for this parameter.
Acceptable	Data within acceptable limits.

These notations can be used as a guideline in evaluating your performance.

Comment Section

This section contains comments submitted to Analytical Products Group by program participants. It also contains comments from APG to participants concerning unusual characteristics of the data set or problems with standards which could influence the interpretation of the data.

Performance Evaluation Summary

This section summarizes performance data in a format similar to the USEPA DMR-QA Report. Detailed information on each parameter is included in the main report.

Certification

This program meets the requirements of the ISO/REMCO Harmonized Protocol for Proficiency Testing of Analytical Laboratories as well as the requirements of ASTM E1301. The statistical techniques used to evaluate the data are consistent with ISO and ASTM guidelines and the National Standards for Water Proficiency Testing Programs. APG is an ISO9001 Certified provider of Proficiency Testing Programs.

Introduction to Laboratory Benchmarking System:

The enclosed report includes a ranking summary of your laboratory's performance in the PT program. Several different measures of performance are provided and each should be interpreted separately. The following sections provide a description of the various ranking methods and their interpretation. These rankings are based upon a broad group of laboratories which analyzed the same samples as your laboratory. Laboratories in the program analyzed the samples as single blind PT samples.

Percent Acceptable Data:

The percent acceptable data is calculated as the percent of actual results reported which were within 99% confidence limits for the parameter. Results are reported for your laboratory and the overall average percent acceptable data achieved by all laboratories.

Rank on Percent Acceptable Data:

This is your laboratory's relative rank out of all possible ranks of in the current study. It should be noted that several laboratories can achieve the same rank. The total number of laboratories reporting data for this study is also reported.

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WP Performance Summary Introduction

Average Percentile

The report inclndes your laboratory's rank on each parameter and the related percentile rank for that parameter. The average percentile is the average of this data across all parameters reported. It is a different measure of performance than percent acceptable data since it is effected by your relative performance on each parameter. The report provides an average for this measure for all laboratories reporting as well as your laboratory's performance.

Weighted Rank on Percent Acceptable

Because the database includes laboratories of many sizes and capabilities, APG has provided a weighted rank based upon percent acceptable. This measure considers the number of parameters which were run by each laboratory and weights the rank by the total number of parameters evaluated.

Weighted Rank on Average Percentile

This measure also considers the number of parameters run by the laboratory. The weighted rank on percentile data considers not only if the analysis was within the limits but also how close to the Mean the reported result was and the total number of analyses run by the laboratory.

Philip C. Coyner
Proficiency Program Manager

Laboratory Benchmark Report

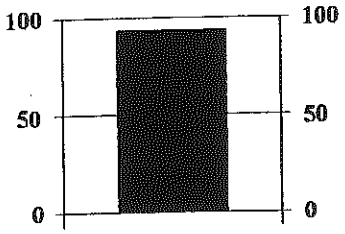
Summary of Ranking Data

Summary of National Ranking Data

Total Number of Laboratories Reporting:	162
Average Percent Acceptable Data:	94.01%
Average Percentile for all Parameters:	61.89%

National Avg % Acceptable

94.0 %

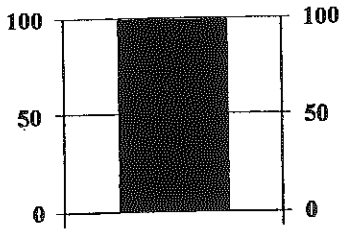


Summary of Laboratory Ranking:

Total Data Points Reported:	287
Number of Acceptable Data Points::	284
Percent Acceptable Data:	98.95%
Average Percentile for all Parameters:	61.82%

Laboratory Avg % Acceptable

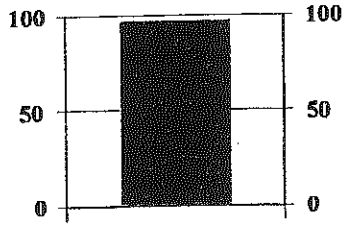
98.95%



Rank on Percent Acceptable Data:	5 of 69
Rank on Average Percentile Data:	94 of 155
Weighted Rank on Percent Acceptable	6 of 89
Weighted Rank on Average Percentile Data:	6 of 159

Weighted Rank Avg Percentile

96.2 %



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Performance Summary

Product: Acid Extractables

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
2,4,6-Trichlorophenol	WP		<5					Acceptable
2,4,6-Trichlorophenol	APG+		<5					Acceptable
2,4-Dichlorophenol	WP		<5					Acceptable
2,4-Dichlorophenol	APG+		<5					Acceptable
2,4-Dimethylphenol	WP		29.496	35	10.1-45.4	0.29		Acceptable
2,4-Dimethylphenol	APG+		100.175	127	17.5-16[illegible]	0.35		Acceptable
2,4-Dinitrophenol	WP		<5					Acceptable
2,4-Dinitrophenol	APG+		<5					Acceptable
2-Chlorophenol	WP		17.7207	20.4	6.91-24.4	0.73		Acceptable
2-Chlorophenol	APG+		154.026	202	56.7-235	0.27		Acceptable
2-Methyl-4,6-Dinitrophenol	WP		72.9093	51.8	9.92-58.1	4.85		**Not Acceptable**
2-Methyl-4,6-Dinitrophenol	APG+		115.878	142	49.6-140	1.38		Acceptable
2-Nitrophenol	WP		21.16	26.1	6.96-33.1	0.27		Acceptable
2-Nitrophenol	APG+		54.829	60.2	20.2-76	0.72		Acceptable
4-Chloro-3-methylphenol	WP		25.4627	32	10.6-40.3	0.007		Acceptable
4-Chloro-3-methylphenol	APG+		50.772	54	35.1-60.1	0.76		Acceptable
4-Nitrophenol	WP		35.395	80.4	0-104	0.19		Acceptable
4-Nitrophenol	APG+		95.857	160	0-175	0.68		Acceptable
Pentachlorophenol	WP		68.1743	72.5	4.58-98.8	1.05		Acceptable
Pentachlorophenol	APG+		140.66	147	33.4-188	1.15		Acceptable
Phenol	WP		21.5643	42.9	0-55	0.15		Acceptable
Phenol	APG+		42.554	76	0-87.7	0.29		Acceptable

Performance Summary

Product: Base Neutral Extractables

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,2,4-Trichlorobenzene	WP		30.578	49.2	11.1-61.7	0.69		Acceptable
1,2,4-Trichlorobenzene	APG+		80.6793	131	15.9-168	0.44		Acceptable
1,2-Dichlorobenzene	WP	94	61.47	64.6	21.3-76.5	1.37		Acceptable
1,2-Dichlorobenzene	APG+	94	104.596	139	38.9-166	0.11		Acceptable
1,3-Dichlorobenzene	WP		39.925	72	16.6-80.9	0.82		Acceptable
1,3-Dichlorobenzene	APG+		115.78	193	24.9-228	0.3		Acceptable
1,4-Dichlorobenzene	WP		26.693	41.1	10.9-48.6	0.48		Acceptable
1,4-Dichlorobenzene	APG+		90.91	111	18.2-141	0.54		Acceptable
2,4-Dinitrotoluene (2,4-DNT)	WP		<5					Acceptable
2,4-Dinitrotoluene (2,4-DNT)	APG+		<5					Acceptable
2,6-Dinitrotoluene (2,6-DNT)	WP		<5					Acceptable
2,6-Dinitrotoluene (2,6-DNT)	APG+		<5					Acceptable
2-Chloronaphthalene	WP		<5					Acceptable
2-Chloronaphthalene	APG+		<5					Acceptable
3,3'-Dichlorobenzidine	WP		<5					Acceptable
3,3'-Dichlorobenzidine	APG+		<5					Acceptable
4-Bromophenyl phenyl ether	WP		<5					Acceptable
4-Bromophenyl phenyl ether	APG+		<5					Acceptable
4-Chlorophenyl phenyl ether	WP		<5					Acceptable
4-Chlorophenyl phenyl ether	APG+		<5					Acceptable
Acenaphthene	WP		<5					Acceptable
Acenaphthene	APG+		<5					Acceptable
Acenaphthylene	WP		<5					Acceptable

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Acenaphthylene	APG+	<5				Acceptable
Anthracene	WP	20.903	25.5	8.4-37.8	0.45	Acceptable
Anthracene	APG+	51.619	56.9	24.3-72.7	0.39	Acceptable
Benzidine	WP	<5				Acceptable
Benzidine	APG+	<5				Acceptable
Benzo(a)anthracene	WP	<5				Acceptable
Benzo(a)anthracene	APG+	<5				Acceptable
Benzo(a)pyrene	WP	<5				Acceptable
Benzo(a)pyrene	APG+	<5				Acceptable
Benzo(b)fluoranthene	WP	<5				Acceptable
Benzo(b)fluoranthene	APG+	<5				Acceptable
Benzo(ghi)perylene	WP	<5				Acceptable
Benzo(ghi)perylene	APG+	<5				Acceptable
Benzo(k)fluoranthene	WP	<5				Acceptable
Benzo(k)fluoranthene	APG+	<5				Acceptable
Bis(2-Chloroethoxy)methane	WP	<5				Acceptable
Bis(2-Chloroethoxy)methane	APG+	<5				Acceptable
Bis(2-Chloroethyl)ether	WP	<5				Acceptable
Bis(2-Chloroethyl)ether	APG+	<5				Acceptable
Bis(2-Chloroisopropyl)ether	WP	<5				Acceptable
Bis(2-Chloroisopropyl)ether	APG+	<5				Acceptable
Bis(2-Ethylhexyl)phthalate	WP	38.432	60.1	18.8-81.9	1.14	Acceptable
Bis(2-Ethylhexyl)phthalate	APG+	82.191	130	51-157	1.24	Acceptable
Butyl benzyl phthalate	WP	32.967	42.4	0-72.1	0.11	Acceptable
Butyl benzyl phthalate	APG+	91.48	118	0-200	0.34	Acceptable
Chrysene	WP	<5				Acceptable
Chrysene	APG+	<5				Acceptable

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Di-n-butyl phthalate	WP	<5				Acceptable
Di-n-butyl phthalate	APG+	<5				Acceptable
Di-n-octyl phthalate	WP	<5				Acceptable
Di-n-octyl phthalate	APG+	<5				Acceptable
Dibenzo(a,h)anthracene	WP	<5				Acceptable
Dibenzo(a,h)anthracene	APG+	<5				Acceptable
Diethyl phthalate	WP	25.263	32.8	0-54.2	0.067	Acceptable
Diethyl phthalate	APG+	105.656	222	0-355	0.37	Acceptable
Dimethyl phthalate	WP	26.649	23.7	8.71-32.5	1.53	Acceptable
Dimethyl phthalate	APG+	146.76	148	0-257	0.84	Acceptable
Fluoranthene	WP	37.69	46.3	26.3-54.4	0.58	Acceptable
Fluoranthene	APG+	85.53	92.9	37.6-119	0.54	Acceptable
Fluorene	WP	28.955	32.2	17.1-39.2	0.23	Acceptable
Fluorene	APG+	77.186	83.3	39.4-103	0.58	Acceptable
Hexachlorobenzene	WP	17.471	21	7.96-26.3	0.089	Acceptable
Hexachlorobenzene	APG+	49.815	52	16.1-71.1	0.68	Acceptable
Hexachlorobutadiene	WP	38.495	44.9	6.95-57.7	0.73	Acceptable
Hexachlorobutadiene	APG+	67.714	78	4.76-109	0.62	Acceptable
Hexachlorocyclopentadiene	WP	16.527	31.8	3.36-36.1	0.58	Acceptable
Hexachlorocyclopentadiene	APG+	71.652	96.9	0-137	0.32	Acceptable
Hexachloroethane	WP	28.386	47	11.3-55.8	0.69	Acceptable
Hexachloroethane	APG+	60.62	83.8	19.5-99.7	0.076	Acceptable
Indeno(1,2,3-cd)pyrene	WP	<5				Acceptable
Indeno(1,2,3-cd)pyrene	APG+	<5				Acceptable
Isophorone	WP	30.806	39.5	15.9-52.1	0.53	Acceptable
Isophorone	APG+	119.416	137	46.4-173	0.45	Acceptable
N-nitrosodi-n-propylamine	WP	<5				Acceptable

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N-nitrosodi-n-propylamine	APG+	<5				Acceptable
N-nitrosodimethylamine	WP	<5				Acceptable
N-nitrosodimethylamine	APG+	<5				Acceptable
N-nitrosodiphenylamine	WP	<5				Acceptable
N-nitrosodiphenylamine	APG+	<5				Acceptable
Naphthalene	WP	22.683	35.2	14.2-41	1.1	Acceptable
Naphthalene	APG+	50.618	67.7	25.3-78	0.12	Acceptable
Nitrobenzene (NB)	WP	27.992	28.5	9.56-38.4	0.83	Acceptable
Nitrobenzene (NB)	APG+	95.638	99.7	32.9-127	1.02	Acceptable
Phenanthrene	WP	34.427	46.8	21.1-56	0.7	Acceptable
Phenanthrene	APG+	123.022	142	46.8-185	0.3	Acceptable
Pyrene	WP	19.591	21.6	10.2-29.6	0.096	Acceptable
Pyrene	APG+	63.723	70.5	36.4-89.4	0.093	Acceptable

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Performance Summary

Study Closing Date 08/16/2000

Product: BTEX

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Benzene	WP		7.8813	7.58	5.13-9.72	0.6		Acceptable
Benzene	APG+		154.9385	143	95.8-179	1.22		Acceptable
Ethylbenzene	WP		9.8017	9.95	6.72-12.9	0.012		Acceptable
Ethylbenzene	APG+		205.8151	200	122-242	1.18		Acceptable
m-Xylene / p-Xylene	WP		6.3907	6.26	3.99-8.8	0.001		Acceptable
m-Xylene / p-Xylene	APG+		56.5302	53.6	40.4-7[illegible]8	0.013		Acceptable
o-Xylene	WP		20.8261	19.9	15.5-24	0.73		Acceptable
o-Xylene	APG+		119.8819	119	108-125	1.03		Acceptable
Toluene	WP		12.6942	12.1	9.09-14.6	0.85		Acceptable
Toluene	APG+		69.5993	66.6	48.2-80.3	0.99		Acceptable
Total Xylenes	WP		27.2168	26.2	19.3-33.2	0.44		Acceptable
Total Xylenes	APG+		176.4121	173	123-221	0.27		Acceptable

Product: Fluoride

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Fluoride	WP	29	1.06475	1.12	0.96-1.28	1.04		Acceptable
Fluoride	APG+	29	12.095	12.5	11-13.8	0.72		Acceptable

APG Customer 1892 Kar Laboratories Inc.
EPA Lab Code MI00041 4425 Manchester Road
Kalamazoo, MI 49001

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WP July 2000
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Product: Minerals

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Alkalinity as CaCO3	WP	27	40	39.1	34.1-44.8	0.34		Acceptable
Alkalinity as CaCO3	APG+	27	60	59.7	53.3-66.3	0.098		Acceptable
Calcium	WP	23	13.96	14	12.3-16.2	0.36		Acceptable
Calcium	APG+	23	7.90	8.01	6.82-9.43	0.51		Acceptable
Chloride	WP	28	68.5	68	61.2-74.5	0.27		Acceptable
Chloride	APG+	28	77	76.6	69.2-83.9	0.2		Acceptable
Conductivity	WP	20	356	373	324-378	0.56		Acceptable
Conductivity	APG+	20	523	542	477-559	0.36		Acceptable
Magnesium	WP	24	7.46	7.15	6.19-8.09	1		Acceptable
Magnesium	APG+	24	10.52	10.7	9.32-12.1	0.39		Acceptable
Potassium	WP	26	7.12	7.37	6.12-8.65	0.64		Acceptable
Potassium	APG+	26	20.62	21	18-24.1	0.43		Acceptable
Sodium	WP	25	35.82	36.6	32.8-40.6	0.68		Acceptable
Sodium	APG+	25	63.15	64.6	58.2-70.9	0.67		Acceptable
Sulfate	WP	30	18.1	17.7	13.6-21.3	0.46		Acceptable
Sulfate	APG+	30	59.2	61.1	50.3-70.3	0.33		Acceptable
Total Dissolved Solids	WP	21	84	187	134-236	5.91		**Not Acceptable**
Total Dissolved Solids	APG+	21	134	282	209-351	6.19		**Not Acceptable**
Total Hardness as CaCO3	WP	22	70.5	64.6	57.1-72.6	2.17		**Check for Error**
Total Hardness as CaCO3	APG+	22	66.5	64.2	56.8-72.2	0.8		Acceptable

APG Customer 1892
EPA Lab Code MI00041

Kar Laboratories Inc.
4425 Manchester Road
Kalamazoo, MI 49001

Performance Summary

Study Closing Date 08/16/2000

Product: PCB's in Oil

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Aroclor 1016/1242 in Oil Sample 1	WP	99	<5					Acceptable
Aroclor 1016/1242 in Oil Sample 2	WP	99	<5					Acceptable
Aroclor 1254 in Oil Sample 1	WP	100	<5					Acceptable
Aroclor 1254 in Oil Sample 2	WP	100	31.6926	42.3	6.97-61.3	0.27		Acceptable
Aroclor 1260 in Oil Sample 1	WP	101	27.5254	38.4	7-54.2	0.39		Acceptable
Aroclor 1260 in Oil Sample 2	WP	101	<5					Acceptable

APG Customer 1892
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Kalamazoo, MI 49001

Performance Summary

Study Closing Date 08/16/2000

Product: PCB's in Water

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Aroclor 1016/1242 Sample 1	WP	40	9.6935	12	3.11-17.1	0.17		Acceptable
Aroclor 1016/1242 Sample 1	APG+	40	4.0706	5.24	1.73-7.18	0.42		Acceptable
Aroclor 1016/1242 Sample 2	WP	40	<0.1					Acceptable
Aroclor 1232 Sample 1	WP	42	<0.1					Acceptable
Aroclor 1232 Sample 1	APG+	42	<0.1					Acceptable
Aroclor 1232 Sample 2	WP	42	<0.1					Acceptable
Aroclor 1248 Sample 1	WP	44	<0.1					Acceptable
Aroclor 1248 Sample 1	APG+	44	<0.1					Acceptable
Aroclor 1248 Sample 2	WP	44	<0.1					Acceptable
Aroclor 1254 Sample 1	WP	45	<0.1					Acceptable
Aroclor 1254 Sample 1	APG+	45	<0.1					Acceptable
Aroclor 1254 Sample 2	WP	45	<0.1					Acceptable
Aroclor 1260 Sample 1	WP	46	<0.1					Acceptable
Aroclor 1260 Sample 1	APG+	46	<0.1					Acceptable
Aroclor 1260 Sample 2	WP	46	8.1667	8.3	4.8-10.7	0.4		Acceptable

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Performance Summary

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Product: Pesticides

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
4,4'-DDD	WP	49	0.2294	0.21	0.088-0.31	0.78		Acceptable
4,4'-DDD	APG+	49	18.5039	19	9.41-26.5	0.2		Acceptable
4,4'-DDE	WP	50	0.3888	0.4	0.18-0.54	0.48		Acceptable
4,4'-DDE	APG+	50	5.6583	6.11	2.91-8.34	0.039		Acceptable
4,4'-DDT	WP	51	0.4508	0.54	0.23-0.75	0.44		Acceptable
4,4'-DDT	APG+	51	14.4765	14.1	6.51-19.1	0.8		Acceptable
Aldrin	WP	47	0.3957	0.48	0.12-0.65	0.067		Acceptable
Aldrin	APG+	47	5.5656	6.79	1.74-9.17	0.088		Acceptable
alpha-BHC	WP		<0.01					Acceptable
alpha-BHC	APG+		<0.01					Acceptable
beta-BHC	WP		<0.01					Acceptable
beta-BHC	APG+		<0.01					Acceptable
delta-BHC	WP		<0.01					Acceptable
delta-BHC	APG+		<0.01					Acceptable
Dieldrin	WP	48	0.2837	0.27	0.14-0.38	0.59		Acceptable
Dieldrin	APG+	48	7.9246	8.27	4.27-11.4	0.074		Acceptable
Endosulfan I	WP		<0.01					Acceptable
Endosulfan I	APG+		<0.01					Acceptable
Endosulfan II	WP		0.3697	0.36	0.22-0.42	1.47		Acceptable
Endosulfan II	APG+		11.3003	11.4	4.95-15.1	0.77		Acceptable
Endosulfan sulfate	WP		<0.01					Acceptable
Endosulfan sulfate	APG+		<0.01					Acceptable
Endrin	WP		<0.01					Acceptable

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Endrin	APG+		<0.01				Acceptable
Endrin aldehyde	WP		<0.01				Acceptable
Endrin aldehyde	APG+		<0.01				Acceptable
gamma-BHC	WP		0.1438	0.16	0.065-0.19	0.67	Acceptable
gamma-BHC	APG+		10.9282	12	8.18-12.7	0.7	Acceptable
Heptachlor	WP	52	0.3499	0.4	0.11-0.56	0.27	Acceptable
Heptachlor	APG+	52	18.7306	20.9	5.47-29.2	0.35	Acceptable
Heptachlor epoxide	WP	78	0.1348	0.14	0.067-0.18	0.79	Acceptable
Heptachlor epoxide	APG+	78	14.3762	14.8	7.56-19	0.56	Acceptable
Methoxychlor	WP		0.2384	0.21	0.087-0.32	0.97	Acceptable
Methoxychlor	APG+		13.8675	13.6	9.16-16.4	0.88	Acceptable

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Product: Polynuclear Aromatic Hydrocarbons

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Acenaphthene	WP		27.651	31.6	6.75-42.1	0.55		Acceptable
Acenaphthylene	WP		<5					Acceptable
Anthracene	WP		39.385	41.8	16-55.7	0.54		Acceptable
Benzo(a)anthracene	WP		<5					Acceptable
Benzo(a)pyrene	WP		<5					Acceptable
Benzo(b)fluoranthene	WP		<5					Acceptable
Benzo(ghi)perylene	WP		<5					Acceptable
Benzo(k)fluoranthene	WP		<5					Acceptable
Chrysene	WP		<5					Acceptable
Dibenzo(a,h)anthracene	WP		<5					Acceptable
Fluoranthene	WP		20.336	22.4	12.1-26.3	0.48		Acceptable
Fluorene	WP		37.672	40.6	10.2-54.1	0.76		Acceptable
Indeno(1,2,3-cd)pyrene	WP		<5					Acceptable
Naphthalene	WP		35.829	44.5	9-54	0.58		Acceptable
Phenanthrene	WP		26.731	34.4	10.8-43.1	0.05		Acceptable
Pyrene	WP		37.504	45.7	16.2-61.2	0.16		Acceptable

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Performance Summary

WP July 2000
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Product: Polynuclear Aromatic Hydrocarbons-PAH

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
Acenaphthene	APG+		58.625	63.5	22.3-88.8	0.27		Acceptable
Acenaphthylene	APG+		<5					Acceptable
Anthracene	APG+		59.568	69.7	16.5-120	0.51		Acceptable
Benzo(a)anthracene	APG+		<5					Acceptable
Benzo(a)pyrene	APG+		<5					Acceptable
Benzo(b)fluoranthene	APG+		<5					Acceptable
Benzo(ghi)perylene	APG+		<5					Acceptable
Benzo(k)fluoranthene	APG+		<5					Acceptable
Chrysene	APG+		<5					Acceptable
Dibenzo(a,h)anthracene	APG+		<5					Acceptable
Fluoranthene	APG+		50.836	50.9	27.9-69.1	0.34		Acceptable
Fluorene	APG+		81.63	85.7	33.9-127	0.06		Acceptable
Indeno(1,2,3-cd)pyrene	APG+		<5					Acceptable
Naphthalene	APG+		63.306	76.9	28.5-99	0.034		Acceptable
Phenanthrene	APG+		91.382	103	39-142	0.051		Acceptable
Pyrene	APG+		86.654	111	36.5-164	0.63		Acceptable

Product: TPH Diesel (DRO)

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
TPH Diesel (DRO)	WP		2.82334	3.02	0-5.16	0.58		Acceptable
TPH Diesel (DRO)	APG+		1.7444	2.01	0-3.36	0.6		Acceptable

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Product: TPH Gasoline (GRO)

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
TPH Gasoline (GRO)	WP		2.012	2.21	0.14-3.84	0.036		Acceptable
TPH Gasoline (GRO)	APG+		2.667	3.06	0.53-4.64	0.13		Acceptable

Analytical Products Group, Inc.
2730 Washington Boulevard • Belpre, Ohio 45714 • 800.272.4442 • Fax 740.423.5588

Performance Summary

Product: Volatiles

Analyte	Product Level	Analyte Code	Reported Value	Assigned Value	Acceptance Range	Z-Score	Test Method	Evaluation
1,1,1-Trichloroethane	WP	56	31.0199	28.2	18.4-37.2	1.03		Acceptable
1,1,1-Trichloroethane	APG+	56	189.3938	187	119-247	0.3		Acceptable
1,1,2,2-Tetrachloroethane	WP		<1					Acceptable
1,1,2,2-Tetrachloroethane	APG+		<1					Acceptable
1,1,2-Trichloroethane	WP		34.2311	32.1	23-38.7	1.28		Acceptable
1,1,2-Trichloroethane	APG+		188.9341	176	115-220	1.2		Acceptable
1,1-Dichloroethane	WP		<1					Acceptable
1,1-Dichloroethane	APG+		<1					Acceptable
1,1-Dichloroethene	WP		16.3626	12.5	6.48-19.8	1.47		Acceptable
1,1-Dichloroethene	APG+		94.9550	80.3	49-125	0.62		Acceptable
1,2-Dichlorobenzene	WP	94	10.1043	9.61	6.41-12.8	0.46		Acceptable
1,2-Dichlorobenzene	APG+	94	64.9907	62.3	44.1-78.5	0.65		Acceptable
1,2-Dichloroethane	WP	54	19.1166	17.4	12.2-23.7	0.64		Acceptable
1,2-Dichloroethane	APG+	54	162.6766	151	104-199	0.69		Acceptable
1,2-Dichloropropane	WP		8.6366	8.16	5.25-10.9	0.6		Acceptable
1,2-Dichloropropane	APG+		126.9083	127	86.5-164	0.15		Acceptable
1,3-Dichlorobenzene	WP	96	11.4482	12	8.21-15.5	0.29		Acceptable
1,3-Dichlorobenzene	APG+	96	103.6579	101	71.9-125	0.58		Acceptable
1,4-Dichlorobenzene	WP	95	15.5367	16.3	11-21.4	0.38		Acceptable
1,4-Dichlorobenzene	APG+	95	78.394	75.1	51.8-96.5	0.57		Acceptable
Benzene	WP	65	18.1212	16.6	11.6-21.8	0.84		Acceptable
Benzene	APG+	65	79.6108	71.4	51.6-91.6	1.2		Acceptable
Bromodichloromethane	WP	60	10.0576	9.18	6.23-12.2	0.86		Acceptable

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Bromodichloromethane	APG+	60	81.3647	76.5	54.4-99.5	0.59	Acceptable
Bromoform	WP	62	42.5665	39.8	25.6-54.6	0.51	Acceptable
Bromoform	APG+	62	114.899	107	70.8-146	0.53	Acceptable
Carbon tetrachloride	WP	58	12.0538	10.9	7.03-15.5	0.61	Acceptable
Carbon tetrachloride	APG+	58	61.8622	53.8	33.2-75.9	1.03	Acceptable
Chlorobenzene	WP	64	27.7123	26.3	18.9-33.3	0.67	Acceptable
Chlorobenzene	APG+	64	128.2946	125	87.1-160	0.41	Acceptable
Chloroform	WP	55	27.1103	23.3	16.4-30.1	1.67	Acceptable
Chloroform	APG+	55	127.1166	120	82.5-153	0.8	Acceptable
cis-1,3-Dichloropropene	WP		<1				Acceptable
cis-1,3-Dichloropropene	APG+		<1				Acceptable
Dibromochloromethane	WP	61	33.4463	30.3	19.1-40.7	0.99	Acceptable
Dibromochloromethane	APG+	61	104.3378	97.4	65.4-127	0.79	Acceptable
Ethylbenzene	WP	66	38.4322	35.1	23.6-45.9	1	Acceptable
Ethylbenzene	APG+	66	139.22	134	88.7-176	0.49	Acceptable
Methylene chloride	WP	63	33.2329	30	19-41.7	0.75	Acceptable
Methylene chloride	APG+	63	113.9205	106	66.8-145	0.63	Acceptable
Tetrachloroethene	WP	59	50.1554	46.6	30.8-59.7	1.01	Acceptable
Tetrachloroethene	APG+	59	160.5351	162	107-206	0.22	Acceptable
Toluene	WP	67	11.4927	10.7	7.36-14	0.72	Acceptable
Toluene	APG+	67	248.2117	240	174-297	0.63	Acceptable
trans-1,2-Dichloroethene	WP		<1				Acceptable
trans-1,2-Dichloroethene	APG+		<1				Acceptable
trans-1,3-Dichloropropene	WP		<1				Acceptable
trans-1,3-Dichloropropene	APG+		<1				Acceptable
Trichloroethene	WP	57	43.0493	40.4	26.3-52.3	0.86	Acceptable
Trichloroethene	APG+	57	88.2876	84.8	54.9-109	0.67	Acceptable

ATTACHMENT A
GROUNDWATER: RESIDENTIAL AND INDUSTRIAL-COMMERCIAL
PART 201 GENERIC CLEANUP CRITERIA AND SCREENING LEVELS

Developed under the authority of the
NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION ACT, 1994 PA 451, AS AMENDED

Groundwater criteria were calculated using currently available chemical-specific data and U.S. Environmental Protection Agency risk assessment guidance. Criteria may change for the next annual revision of the criteria tables. All criteria are expressed in units of parts per billion (ppb;ug/L). Scientific notation is represented by E+ or E- a value; for example, 2 x 10^6 is reported as 2.0E+6. For comparison to the criteria, groundwater samples should be representative of the water moving through the aquifer in the contaminant plume. Samples should be collected using a low flow protocol that minimizes turbidity caused by disturbances from sampling and, in most cases, total analyses of the samples should be conducted (see Op Memos #18 for details). Please refer to Op Memo #6 for recommended analytical methods and target detection limits.

Guidesheet Number →		#1	#2	#3	#4	#5	#6	#7	#8	#9
	Chemical Abstract Service Number	Residential & Commercial I Drinking Water Criteria	Industrial & Commercial II, III & IV Drinking Water Criteria	Groundwater Surface Water Interface Criteria	Residential & Commercial I Groundwater Volatilization to Indoor Air Inhalation Criteria	Industrial & Commercial II, III & IV Groundwater Volatilization to Indoor Air Inhalation Criteria	Groundwater Contact Criteria	Water Solubility	Flammability and Explosivity Screening Level	Acute Inhalation Screening Level
PHYSICAL PARAMETERS										
Dissolved oxygen (DO)		NA	NA	(AE)	NA	NA	NA	NA	NA	NA
Phosphorus		NA	NA	(AE)	NA	NA	NA	NA	NA	NA
Total dissolved solids (TDS)		5.0E+5 (E)	5.0E+5 (E)	(AE)	NA	NA	NA	NA	NA	NA
HAZARDOUS SUBSTANCES										
Acenaphthene	83329	1,300	3,800	19	4,200 (S)	4,200 (S)	4,200 (S)	4,240	ID	ID
Acenaphthylene	208968	52	150	ID	3,900 (S)	3,900 (S)	3,900 (S)	3,930	ID	ID
Acetaldehyde (I)	75070	950	2,700	NA	1.1E+6	2.3E+6	4.2E+7	1.0E+9	4.4E+6	2.6E+7
Acetic acid	64197	18,000 (M)	18,000 (M)	18,000 (M)	NLV	NLV	1.8E+8	6.0E+9	4.8E+9	1.0E+9 (D)
Acetone (I)	67641	730	2,100	1,700	1.0E+9 (D,S)	1.0E+9 (D,S)	3.1E+7	1.0E+9	7.5E+6	1.0E+9 (D)
Acetonitrile	75058	140	400	NA	2.4E+7	4.5E+7	5.6E+6	2.00E+8	1.0E+7	2.0E+8
Acetophenone	98862	1,500	4,400	NA	6.1E+6 (S)	6.1E+6 (S)	6.1E+6 (S)	6.1E+6	ID	ID
Acrolein (I)	107028	120	330	NA	2,100	4,200	3.4E+6	2.10E+8	3.3E+6	3.4E+5
Acrylamide	79061	0.3	1.2	NA	NLV	NLV	13,000	2.20E+9	NA	ID
Acrylic acid	79107	3,900	11,000	NA	1.2E+7	2.8E+7	7.6E+7	1.00E+9	1.0E+9 (D)	ID
Acrylonitrile (I)	107131	2.6	11	4.9 (X)	34,000	1.9E+5	14,000	7.50E+7	3.2E+6	ID
Alachlor	15972608	2.0 (A)	2.0 (A)	11 (X)	NLV	NLV	1,700	1.83E+5	ID	ID
Aldicarb	116063	3.0 (A)	3.0 (A)	NA	NLV	NLV	1.2E+5	6.00E+6	ID	ID
Aldicarb sulfoxide	1646873	4.0 (A)	4.0 (A)	NA	NLV	NLV	2.7E+6	2.80E+7	ID	ID
Aldicarb sulfone	1646884	2.0 (A)	2.0 (A)	NA	NLV	NLV	2.1E+6	7.80E+6	ID	ID
Aldrin	309002	0.098	0.4	NA	180 (S)	180 (S)	0.34 (AA)	180	ID	ID
Aluminum (B)	7429905	50 (V)	50 (V)	NA	NLV	NLV	6.4E+7	NA	ID	ID
Ammonia	7664417	10,000 (N)	10,000 (N)	(AC)	3.2E+6	7.2E+6	ID	5.30E+8	ID	3.5E+6

ATTACHMENT A
GROUNDWATER: RESIDENTIAL AND INDUSTRIAL-COMMERCIAL
PART 201 GENERIC CLEANUP CRITERIA AND SCREENING LEVELS

Guidesheet Number →		#1	#2	#3	#4	#5	#6	#7	#8	#9
	Chemical Abstract Service Number	Residential & Commercial I Drinking Water Criteria	Industrial & Commercial II, III & IV Drinking Water Criteria	Groundwater Surface Water Interface Criteria	Residential & Commercial I Groundwater Volatilization to Indoor Air Inhalation Criteria	Industrial & Commercial II, III & IV Groundwater Volatilization to Indoor Air Inhalation Criteria	Groundwater Contact Criteria	Water Solubility	Flammability and Explosivity Screening Level	Acute Inhalation Screening Level
Aniline	62533	53	220	20 {M}	NLV	NLV	1.4E+5	3.60E+7	NA	ID
Anthracene	120127	43 {S}	43 {S}	ID	43 {S}	43 {S}	43 {S}	43.4	ID	ID
Antimony	7440360	6.0 {A}	6.0 {A}	ID	NLV	NLV	68,000	NA	ID	ID
Arsenic {B}	7440382	50 {A}	50 {A}	150 {X}	NLV	NLV	4,300	NA	ID	ID
Asbestos {AB}	1332214	7.0E+6 f/mL {A}	7.0E+6 f/mL {A}	NA	NLV	NLV	ID	NA	NA	ID
Atrazine	1912249	3.0 {A}	3.0 {A}	7.3 {X}	NLV	NLV	5,400	70,000	ID	ID
Azobenzene	103333	23	94	NA	6,400 {S}	6,400 {S}	1,600	6,400	ID	ID
Barium	7440393	2,000 {A}	2,000 {A}	{G,X}	NLV	NLV	1.4E+7	NA	ID	ID
Benzene {I}	71432	5.0 {A}	5.0 {A}	200 {X}	5,600	36,000	11,000	1.75E+6	34,000	67,000
Benzidine	92875	0.3 {M}	0.3 {M}	ID	NLV	NLV	7.1	5.20E+5	ID	ID
Benzo(a)anthracene {Q}	56553	2.1	8.5	NA	NLV	NLV	9.4 {S,AA}	9.4	ID	ID
Benzo(b)fluoranthene {Q}	205992	2.0 {M}	2.0 {M}	ID	NLV	NLV	2.0 {M,AA}	1.5	ID	ID
Benzo(k)fluoranthene {Q}	207089	5.0 {M}	5.0 {M}	NA	NLV	NLV	5.0 {M,AA}	0.8	ID	ID
Benzo(g,h,i)perylene	191242	5.0 {M}	5.0 {M}	NA	NLV	NLV	5.0 {M,AA}	0.26	ID	ID
Benzo(a)pyrene {Q}	50328	5.0 {A,M}	5.0 {A,M}	ID	NLV	NLV	5.0 {M,AA}	1.62	ID	ID
Benzoic acid	65850	32,000	92,000	NA	NLV	NLV	3.5E+6 {S}	3.50E+6	ID	ID
Benzyl alcohol	100516	10,000	29,000	NA	NLV	NLV	4.4E+7 {S}	4.40E+7	ID	ID
Benzyl chloride	100447	7.7	32	NA	12,000	77,000	3,600	4.90E+5	NA	ID
Beryllium	7440417	4.0 {A}	4.0 {A}	{G}	NLV	NLV	2.9E+5	NA	ID	ID
bis(2-Chloroethoxy)ethane	112265	ID	ID	NA	NLV	NLV	ID	1.89E+7	ID	ID
bis(2-Chloroethyl)ether {I}	111444	2.0	8.3	NA	38,000	2.1E+5	5,700	1.72E+7	1.7E+7 {S}	1.7E+7 {S}
bis(2-Ethylhexyl)phthalate	117817	6.0 {A}	6.0 {A}	32	NLV	NLV	320 {AA}	340	NA	340 {S}
Boron {B}	7440428	500 {F}	500 {F}	1,900	NLV	NLV	6.2E+7	NA	ID	ID
Bromobenzene {I}	108861	18	50	NA	1.8E+5	3.9E+5	12,000	4.13E+5	ID	ID
Bromodichloromethane	75274	100 {A,W}	100 {A,W}	ID	4,800	38,000	14,000	6.74E+6	ID	ID
Bromoform	75252	100 {A,W}	100 {A,W}	ID	4.8E+5	3.1E+6 {S}	1.4E+5	3.10E+6	ID	ID
Bromomethane	74839	10	29	35	4,000	9,000	70,000	1.45E+7	ID	ID

KAR LABORATORIES, INC.

CORRECTIVE ACTION PROTOCOL

Laboratory Corrective Action

Each Laboratory Section Supervisor is responsible for the initiation of all corrective action processes performed within their Section. The KAR Quality Assurance Officer (QAO) is responsible for the coordination/oversight and documentation of all such activity. The QAO is also responsible for final approval of any corrective action ultimately taken. Documentation will include details of the problem encountered, the name and affiliation of any person contacted regarding the problem, and action taken in an effort to correct the problem. The QAO will also record details regarding the outcome of any corrective action/problem resolution and initiate any procedural changes deemed necessary. A copy of KAR's Corrective Action Report is attached.

In the case of instrument failure or procedural problems, the analyst is responsible for terminating the analytical run and contacting the Laboratory Section Supervisor. The problem will then be evaluated through consultation with the QAO and the appropriate corrective action taken. Analyses will resume when proper operation of the instrument is confirmed. The QAO is responsible for documentation and implementation of the corrective action.

As part of the data validation process, the KAR QAO will initiate corrective action when reported results exceed acceptance limits or when the QC requirements for a given analysis are not satisfied.

When the deviation is known to have a definite effect on data quality, the QAO will automatically reject the data and activate re-entry of the samples into the system for re-analysis. The appropriate laboratory personnel will be informed of the reasons for re-analysis and appropriate QC protocol to be reviewed.

In some cases, however, the QAO may choose to confer with the FTC&H Project Manager as to the actual effect of the deviation on data usage. The FTC&H Project Manager will notify the Technical Reviewers of the situation and the effect of the deviation. The Technical Reviewers will make a decision on the corrective action necessary and submit a memorandum to the FTC&H Project Manager and the KAR QAO on the necessary steps to be taken.

The KAR QAO will then appropriately flag or reject the affected data. Data flagged as estimated will be reported as such, and a case narrative describing deviation will be included in the laboratory data package.

When data is rejected, the KAR QAO will trigger the re-entry of the samples into the system.

KAR LABORATORIES, INC.
CORRECTIVE ACTION REPORT

Report Date	
Test	
Analysis Date	
Analyst	
KAR Sample ID	

Corrective action required	
Reviewed by:	/ (signature/date)

Sample preparation	
Completed by:	/ (signature/date)

Reanalysis	
Completed by:	/ (signature/date)

Quality control review	
Data released by:	/ (signature/date)

TRIMATRIX LABORATORIES, INC.

CHAIN-OF-CUSTODY PROTOCOL

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

INTERNAL CHAIN-OF-CUSTODY PROCEDURE

UNCONTROLLED DOCUMENT

APPROVALS:

QA Manager: _____ Date: 6/9/98
Rick D. Wilburn

Laboratory Manager: _____ Date: 6/9/98
Douglas E. Kriscunas

Procedure Number: GR-10-104
Revision Number: 2.0

Date Initiated: 8/30/96
Effective Date: 5/22/98

Date Revised: 5/22/98
Pages Revised: All

By: Douglas E. Kriscunas

Total Number of Pages: 7

1.0 SUMMARY OF PROCEDURE

1.1 This SOP establishes uniform policies for a legally-defensible internal chain-of-custody (COC) system for samples requiring a defined level of security. Following these guidelines should provide unbroken tracking of samples from the client source, through the analytical process, to final sample disposition. This procedure also includes the general security measures taken to ensure laboratory integrity is maintained for all analytical areas.

2.0 DETAILED PROCEDURE

2.1 Upon receipt and proper acknowledgment of a cooler containing samples designated as internal chain of custody (COC), the sample technicians must perform a thorough inspection of any custody seals. Should any of the seals arrive damaged, the project chemist and/or the internal client contact must be immediately contacted.

2.2 All paperwork accompanying the sample cooler must be retrieved and checked for completeness and accuracy. Any discrepancies between the received samples and the shipping papers or the project information must be noted. The project chemist must be informed of the problems, and action taken to explain and correct the errors.

2.3 Only when the samples have been properly accounted for and any discrepancies resolved may they be logged into LIMS. During the log-in process, the option to designate the samples as Internal Chain-of-Custody must be selected. This will initiate the creation of sign-out sheets for each analysis the samples are logged in for (Attachment 1).

2.4 After log-in, the samples will be moved to their designated storage areas and placed on the appropriate shelves (Attachment 2). Access to all sample storage areas is limited to employees only.

2.5 The sign-out sheets are placed in folders located in the laboratory by the walk-in cooler. The sample technicians will ensure each sample has the appropriate type and number of sign-out sheets.

2.6 The incoming samples COC status is communicated to the laboratory areas through the use of arrival logs, worklists, and benchsheets, each of which are generated by LIMS. In addition, managers and group leaders must make sure the chemists and technicians are aware of the COC status of the samples, and that sign-out procedures are strictly followed.

2.7 When preparing to analyze internal COC samples, the sign-out sheet must be completely filled out with removal time, analyst name, and return time. The internal COC forms are filled out each time the samples are removed form their designated storage area. Interim sample storage areas are present in each laboratory area, for use on in-process samples. These storage areas also have access limited to employees only. After signing the samples out from their designated storage area, the samples may be stored in these areas until analyses are complete. Once complete, the samples must be returned to their original location, and the paperwork completed before the analyst may proceed to any other task.

2.8 When the submittal has been completed, the project chemist must review the contents of the COC folder for each submittal. The project chemist will check the COCs for completeness and then include the paperwork in the project folder.

3.0 REPORTING AND DELIVERABLES

3.1 Examples of all reporting and deliverable requirements are covered in the Attachment/Appendixes section of this SOP, and in the associated analytical SOPs.

4.0 QUALITY ASSURANCE

4.1 All laboratory quality assurance activities as outlined in the TriMatrix Quality Assurance Manual, and as specified in any related Standard Operating Procedures, must be followed.

4.2 The laboratory is a restricted access area. Only authorized personnel are allowed into the laboratory without escorts. Visitors must sign the Visitor Logbook when entering and exiting the laboratory.

4.3 All access doors are secured with electronic keycode locks. Periodic changes in the random access codes are performed to minimize any unauthorized entrance.

4.4 The project chemists is responsible for communicating COC sample information to the sample technicians when this knowledge is available. The project chemist is also responsible for monitoring the progress of the submittal, collecting the COC sign-out sheets when the analyses are completed, and checking each COC for completeness.

4.5 Sample technicians are responsible for receiving, inspecting, and logging in the samples correctly for COC status, and printing and placing sign-out sheets into folders

4.6 Chemists and analysts must strictly follow protocol when performing analyses on COC samples. Each time a sample is removed from its primary storage area, the sign-out sheet must be filled in, including the removal time, return time and a signature, in order to comply with legal integrity standards.

4.7 Laboratory managers and group leaders are responsible for making sure their area chemists are following the COC procedures.

4.8 The overall internal chain-of-custody flow (Attachment 3).

5.0 REFERENCES

5.1 TriMatrix Quality Assurance Manual, current revision.

Approved By: 6/9/98 **Approved By:** 6/9/98
QA Manager **Area Manager**

6.0 ATTACHMENTS/APPENDICES

6.1 Internal Chain-of-Custody Example

6.2 Secure Sample Storage Area Locations

6.3 Laboratory Internal Chain-of-Custody Flow

Approved By: 6/9/98 **Approved By:** 6/9/98

QA Manager **Area Manager**

Attachment 1
Internal Chain-of-Custody Example

19-MAY-1998

TRIMATRIX LABORATORIES, INC.
CHAIN OF CUSTODY REPORT FOR AN ENTIRE SUBMITTAL

PAGE #34

CLIENT: [redacted] PROJECT: [redacted]

SUBMITTAL: May 18, 1998 Samples PROJECT: 33416-13

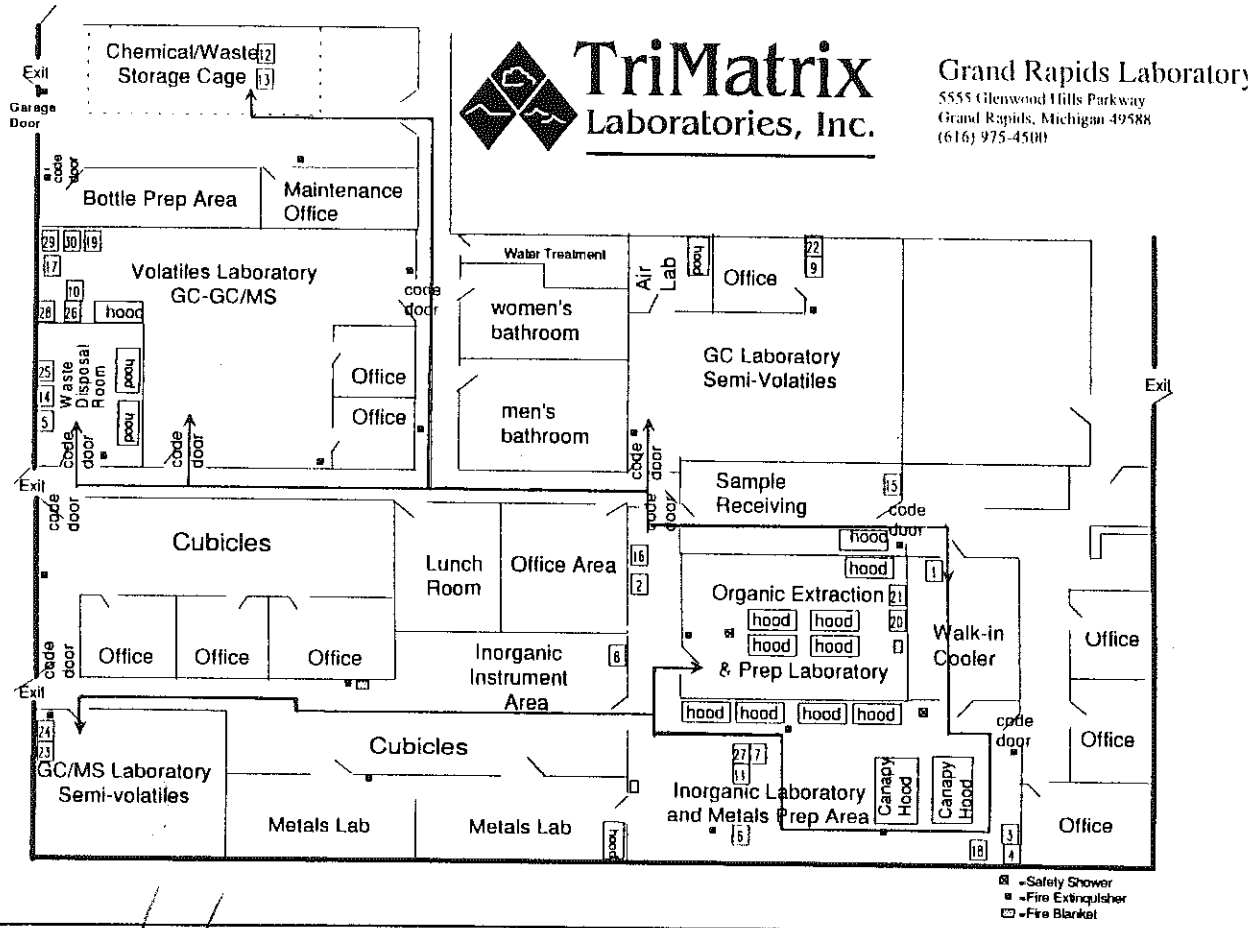
Parameter: EXTRACT: 8270-B/N/A Method: EXT/LQ-LQ/WTR Ref Cit: USEPA-3510B Matrix: WATER

SAMPLE #	REMOVED BY: (SIGNATURE)	DATE & TIME REMOVED	RELINQUISHED BY: DATE & TIME	RECEIVED BY: DATE & TIME	DATE & TIME RETURNED
196850					
196851					
196852					
196853					
196854					
196855					
196856					
196857					
196858					
196859					

Approved By: 6/9/98
QA Manager

Approved By: 6/9/98
Area Manager

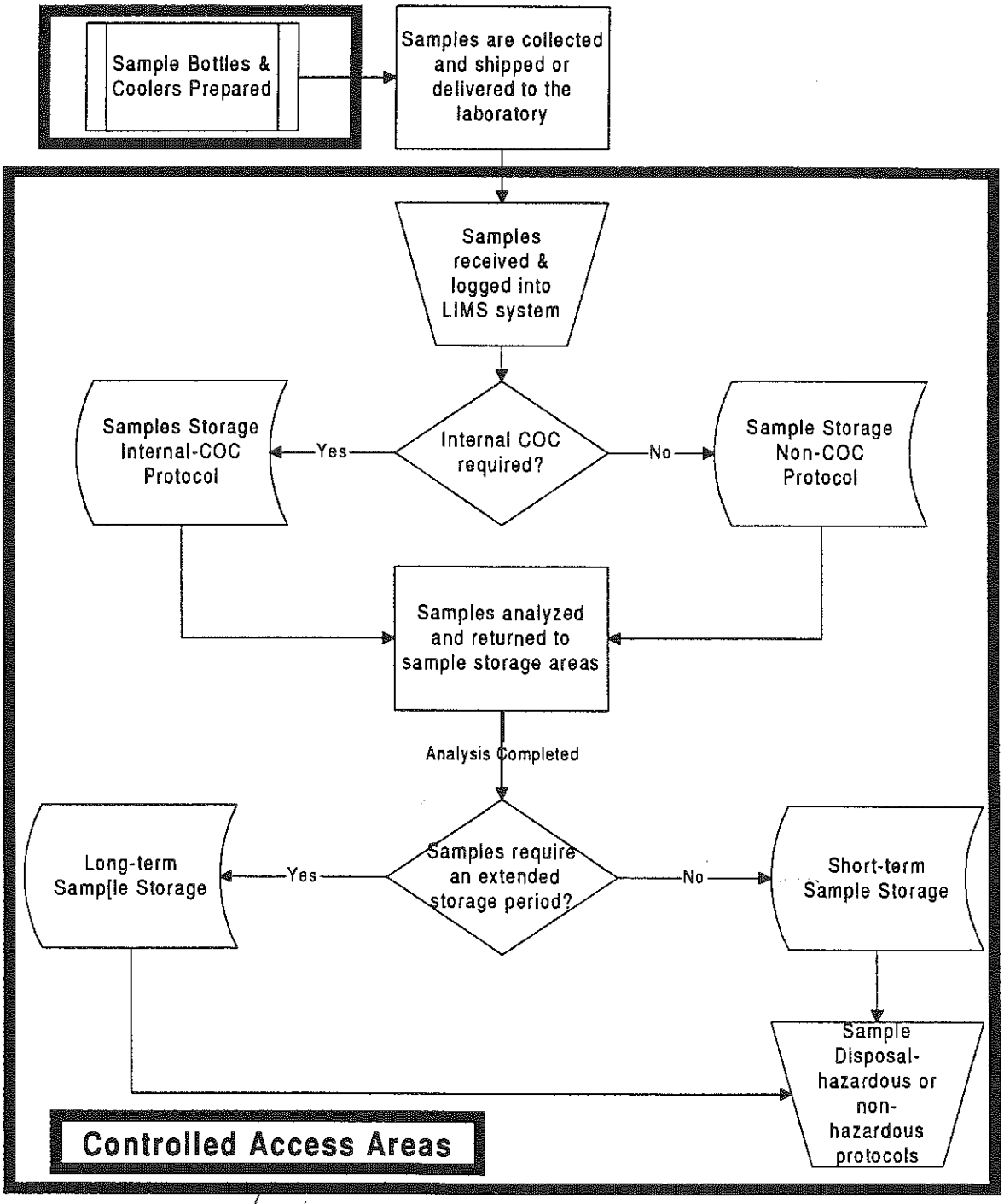
Attachment 2
Secure Sample Storage Area Locations



Approved By: 6/9/98
QA Manager

Approved By: 6/9/98
Area Manager

Attachment 3
Laboratory Internal Chain-of-Custody Flow



Approved By: 6/9/98 QA Manager

Approved By: 6/9/98 Area Manager

TRIMATRIX LABORATORIES, INC.

ANALYTICAL METHODS

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

PERKIN ELMER ELAN-6000

USEPA METHODS 6020/200.8

UNCONTROLLED DOCUMENT

APPROVALS:

Inorganic Manager: _____ Date: 11/23/98
Douglas E. Kriscunas

QA Manager: _____ Date: 11/23/98
Rick D. Wilburn

Laboratory Manager: _____ Date: 11/23/98
Douglas E. Kriscunas

Procedure Number: GR-01-129
Revision Number: 2.1

Date Initiated: 12/4/97
Effective Date: 11/23/98

Date Revised: 11/23/98
Pages Revised: 2,16,29

By: David W. Johnson

Total Number of Pages: 30

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma mass spectrometry (ICP-MS) is a relatively new methodology applicable to a large range of metallic elements in numerous matrices, including, but not limited to: soil, water, drinking water, wastewater, TCLP extracts, EPTox extracts, ASTM extracts, oil, solvents, sludge, air, pure products, and other matrices that may be extracted or dissolved into an acidic aqueous solution. Most matrices require solubilization or digestion prior to analysis.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 0, September, 1994, Inductively Coupled Plasma-Mass Spectrometry.

2.2 *Methods for the Determination of Metals in Environmental Samples,* Supplement I, May 1994, Revision 5.4, EMMC Version, May 1994, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry".

3.0 SUMMARY OF PROCEDURE

3.1 Prior to analysis, the sample must be solubilized or digested using an appropriate sample preparation method. See Methods 3005-3050/200.0.

3.2 This method describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio frequency inductively coupled plasma. Sample material in solution is introduced by pneumatic nebulization into radio-frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole are detected by an electron multiplier or Faraday detector and the ion information processed by a data handling system.

3.3 Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards.

4.0 PARAMETER OR COMPOUND LIST

4.1 This method may be used for the analysis of the following metals.

Aluminum	Molybdenum
Antimony	Nickel
Arsenic	Selenium
Barium	Silver

Beryllium
Cadmium
Chromium
Cobalt
Copper
Lead
Manganese
Thallium
Vanadium
Zinc

5.0 REFERENCED SOPs

5.1 None referenced with regards to the analysis, however all applicable digestion SOPs would be required to pretreat the samples.

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, analysis using another verified and documented isotope, or use of another method. Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

6.1.1 Isobaric elemental interferences - Are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

6.1.2 Isobaric polyatomic ion interferences - Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Such interferences must be

recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the corrections for data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions. In particular, the common ^{82}Kr interference that affects the determination of both arsenic and selenium, can be greatly reduced with the use of high purity krypton free argon.

6.1.3 Abundance sensitivity - Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operatmg pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

6.1.4 Memory interferences - Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected the sample should be reanalyzed after a long rinse period. In the determination of mercury, which suffers from severe memory effects, the addition of 100 ug/L gold will effectively rinse 5 ug/L mercury in approximately 2 minutes. Higher concentration will require a longer rinse time.

6.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<2 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

corrected arsenic signal (using natural isotope abundances for coefficient approximations) =

[(m/z 75 signal) - ((3.13)(m/z 77 signal)) + ((2.73)(m/z 82 signal))]

where the final term ((2.73)(m/z 82 signal)) adjusts for any selenium contribution at m/z 77

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are ONLY illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for the standard solution at a concentration providing suitable (<1 percent) counting precision.

6.2.1 The accuracy of these types of equations are based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide as the interferent. This type of correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis can be met.

6.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2%(2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of an internal standard is less than 70 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

6.4 Memory interferences can occur when there are large concentration differences between samples or standards, which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

7.0 SAFETY PRECAUTIONS

7.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the "TriMatrix Laboratory Safety Manual".

7.2 Concentrated acids are used in the preparation of standards and samples for analysis by ICP-MS. Gloves and safety glasses must be worn at all times when handling concentrated acids. Gloves must also be worn when handling digested samples. Please refer to the MSDS for information on these or any other chemicals utilized in this procedure.

7.3 Check the exhaust hood over the instrument to be sure it is operating correctly. If the ventilation system is not working properly, extinguish the plasma if lit and immediately contact the metals lab manager. Under no circumstances should the ICP-MS be used if the exhaust hood is not working.

7.4 UV protective glasses must be worn at all times in the metals laboratory. The plasma emits UV radiation. Avoid looking directly at the plasma without some type of strong UV protection. The instrument uses a very UV resistant material in the viewing port as the analyst may watch the plasma. Do not tamper with this plate. Do not operate the machine without this plate in place. Do not attempt to view the plasma directly or indirectly in any way. Failure to follow this policy may cause very serious and immediate damage to the retina of the eye.

7.5 The ICP-MS emits a strong Rf field. To minimize exposure to this field, Perkin Elmer has included several safety interlocks to prevent direct exposure of the analyst to harmful radiation. Never override any interlock on the ICP-MS. When working on the instrument, always replace all of the Rf shielding using all of the supplied screws. If any safety device has been tampered with, contact the metals lab manager.

7.6 The ICP uses Ar to sustain the plasma and to nebulize sample into the plasma. Although Ar in and of itself is not hazardous or flammable, it may cause suffocation through oxygen deprivation. It is therefore imperative that all sources of Ar be turned off with a valve when not in use. Since Ar is colorless and odorless, if you feel lightheaded, please evacuate the metals lab at once and notify the metals lab manager. Please refer to the MSDS for information on this or any chemicals utilized in this procedure.

7.7 Many of the elements used in the procedure are toxic if ingested. Please refer to the MSDS for information on these or any other chemicals utilized in this procedure.

7.8 No food or drink is allowed in the metals lab. Food or drink may become contaminated with acid or metals and may therefore be hazardous.

7.9 Wash hands before starting work. Chemicals may be present on the skin which may interfere with metals analysis. Wash hands before leaving the metals lab. Chemicals and acids may be on the skin that could eventually be ingested or passed on to a second party through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Aqueous samples must be acidified at the time of collection to a pH of <2.

8.2 Solid samples require no preservation for metals.

8.3 All samples may be collected in glass or plastic. If Silicon or Boron is to be analyzed, plastic containers must be used. The acidified sample must never come into contact with any metal as this would cause leaching of the metal into the sample.

8.4 For the analysis of dissolved metals, the sample should be filtered on site and then acidified to a pH of <2.

8.5 Holding times for all metals for ICP analysis is 180 days. In the case of TCLP or similar extracts, the hold time starts at the time of filtration.

8.6 The minimum sample size for this method is 3 ml of aqueous sample per metal to be analyzed. This implies that the sample must be solubilized prior to analysis. A smaller minimum amount may be used if the sample will be diluted at the sacrifice of the detection limit.

8.7 Digested (solubilized) samples and undigested acidified aqueous samples need not be refrigerated. Solid samples should be refrigerated so that other parameters may be performed on them. All samples must be at room temperature prior to analysis.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Inductively coupled plasma mass spectrometer:

9.1.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system. The instrument should also include data system that will allow corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

NOTE: If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result.

9.1.2 Radio-frequency generator compliant with FCC regulations.

9.1.3 Argon gas supply - High purity grade (99.99%). When analysis are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders (Section 4.1.3).

9.1.4 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.

9.1.5 A mass-flow controller on the nebulizer gas supply is required.

9.2 Analytical balance, with the capability of measuring to 0.1 mg for use in weighing solids, for preparing standards, and for determining dissolved solids in digestates or extracts.

9.3 A temperature adjustable hot plate capable of maintaining a temperature of 95° C.

9.4 Recirculator/chiller, Neslab CFT750 or equivalent. Temperature should be maintained at 18° C and pressure should be at 35-60 psi. The recirculator is attached directly to the mass spectrometer to maintain isothermal conditions.

9.5 15 ml clear centrifuge tubes or equivalent. Tubes should stand upright within the autosampler rack without tipping or leaning.

9.6 Eppendorf auto-pipettors capable of delivering 5-1000 ul.

9.7 Class A volumetric flasks, various volumes.

9.8 Class A reusable pipettes, various volumes.

9.9 (optional) An air displacement pipettor capable of delivering volumes ranging from 0.1 to 2500 ul with an assortment of high quality disposable pipette tips.

9.10 Mortar and pestle, ceramic or nonmetallic material.

9.11 Polypropylene sieve, 5-mesh (4 mm opening).

9.12 A gravity convection drying oven with thermostatic control capable of maintaining 105° C $\pm$ 5° C.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 All maintenance activities must be recorded in the instrument maintenance, or instrument run logbook. Daily maintenance activities are recorded in the run logbook. All other maintenance activities must be recorded in the instrument maintenance logbook.

10.2 At the beginning of each shift (every 8 hours) the manifold pump tubing must be replaced. This must be recorded in the instrument run logbook.

10.3 There are 2 filters on the ELAN 6000 that must be replaced periodically. The two filters are located on the back of the instrument. This must be noted in the instrument maintenance logbook.

10.4 Inspect the Ar supply when the shift begins. If the liquid level of the Ar falls below the re-order mark, notify the person responsible for ordering gasses or the metals manager. This must be recorded in the instrument run logbook.

10.5 Inspect the water container on the floor alongside the instrument every shift. If the jug is full, properly dispose of the liquid. This must be recorded in the instrument run logbook.

10.6 Visually inspect the torch before lighting the instrument. Do not touch or move the torch. The inspection should be visible only. This must be recorded in the instrument run logbook.

10.6.1 Open the vacuum chamber.

10.6.2 Observe the torch. If the torch is broken or cracked, replace it. See section 10.7 for a discussion on how to disassemble the torch and assembly.

10.6.3 Listen for any obvious leaks in the Ar lines going to the torch and nebulizer. If leaks are heard, investigate them and tighten the fittings to stop the leak. If the leak cannot be found or cannot be stopped, contact the metals lab manager.

10.7 Once every four to eight weeks disassemble the entire torch assembly and inspect all parts for wear. Replace all worn or damaged parts. Record all changes in the instrument maintenance logbook.

10.7.1 Turn off the plasma if it is on by selecting instrument, front panel, and then stop on the plasma box. The pump will stop when the plasma is extinguished.

10.7.2 Turn off the RF Generator by turning off the circuit breaker labeled RF Generator (CB1) on the left side of the instrument.

10.7.3 Loosen the retaining ring and remove the spray chamber assembly.

10.7.4 Open the top left cover of the ELAN 6000. Use a flat blade screw driver on the release mechanism to release the vacuum chamber interlock lever. Grasp the lever and pull in counter clockwise direction to slide the vacuum chamber and interface away from the torch box.

10.7.5 Remove the gas line connections from the ICP torch by loosening the Swagelock fittings. Then slide the fittings and connection tubing up and off of the ICP torch.

10.7.6 To remove the torch assembly, rotate the torch mount 1/8 turn counter clockwise and remove the entire assembly through the right side of the torch box.

10.7.7 With one hand grasping the ICP torch and the other holding onto the lexan adapter, twist and pull back on the adapter to separate the adapter from the torch.

10.7.8 Inspect all O-rings and replace any that are cracked or damaged. Record in maintenance log book.

10.7.9 Remove the Alumina injector. If it is dirty wash it with soap and water, dry, then put in the muffle furnace at 700° C for 20 min.

10.7.10 If the torch is dirty immerse it in an ultrasonic cleaner containing 1% nitric acid. Rinse with deionized water. If the torch cannot be cleaned or is damaged, replace.

10.7.11 After the torch has been cleaned or replaced, follow these steps to reposition and align the ICP torch.

10.7.11.1 Slide the injector/support adapter to the back of the torch.

10.7.11.2 Place the torch through the hole in the right side of the torch box. Rotate the torch assembly 1/8 turn clockwise until the bayonet mount is fully seated.

10.7.11.3 Reattach the gas lines to the ICP torch. Slide both the fittings and connecting tubing onto the torch and tighten the Swagelock fittings several turns.

10.7.11.4 To check the position and measure for the proper alignment of the torch follow steps 10.7.11.5 through 8.

10.7.11.5 Place the torch alignment tool on the torch so that the flange of the alignment tool touches the first turn of the load coil. Loosen the torch locking collar approximately 1 cm and slide the torch so that it is lined up with the outer edge of the torch.

10.7.11.6 Slide the tool out approximately 1/2 inch and, using the lever, move the vacuum chamber interlock into the lock position.

10.7.11.7 Move the vacuum chamber to the closed position to locate the alignment tool within the load coil.

10.7.11.8 Move the chamber to the open position and adjust the vacuum chamber position so the top end of the torch is even with the 5.5 mm cutout depth of the alignment tool.

10.7.11.9 If the torch is not properly lined up, loosen the two locking screws of the vacuum chamber interlock. Adjust the vacuum chamber forwards or backwards until the proper position is achieved.

10.7.11.10 Slide the vacuum chamber and interface toward the torch box. Secure the vacuum chamber interlock and close the top cover.

10.7.11.11 Turn on the RF Generator by turning on the circuit breaker labeled ICP Power (CB1) on the side of the instrument.

10.7.12 Inspect the drain line at the base of the spray chamber. There should be no leaks or cracks in the tubing. If a problem exists, replace the O-ring in the drain cap. This must be recorded in the instrument maintenance logbook.

10.7.13 Inspect the nebulizer for wear. This must be recorded in the instrument run logbook.

10.7.13.1 Salt deposits, if present, should be removed with water. Record any actions in the instrument maintenance logbook.

10.7.13.2 If a cross-flow nebulizer is used, check the tips for wear. Replace the tips if excessive wear is noted. Record any actions in the instrument maintenance logbook.

10.8 Inspect the printing quality of the printer. If the print is hard to read or light in appearance, replace the printer cartridge with the appropriate replacement.

11.0 CHEMICALS AND REAGENTS

11.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Redistilled acids may be used if it has been demonstrated that the acid is free from contamination.

11.1.1 Concentrated Nitric acid, trace metal grade (Fisher Cat #A509-212).

11.1.2 Nitric acid, trace metals grade (1:1): Add 500 ml concentrated HNO_3 to 400 ml ASTM Type II water. Cool. Dilute to 1L.

11.2 ASTM Type II water (ASTM D1193). Deionized water is fed into a Barnstead Model FI-STREEM 2 all glass distillation unit. The resulting distillate is immediately placed into a plastic container. Impurities are measured by the Inorganic group at TriMatrix. This is the only water acceptable for use in the Metals lab for dilutions or standard preparation.

11.3 Standard stock solutions are purchased primarily form Inorganic Ventures. All stock solutions are ICP grade single-element solutions at concentrations of 1000 or 10,000 ppm.

11.4 Argon gas supply: Welding grade or better. This is plumbed from a liquid argon tank located outside of the building. Ar is used as the main plasma gas, the auxiliary plasma gas, the nebulizer carrier gas, and the Rf coil coolant.

12.0 STANDARDS PREPARATION

12.1 All standards should be prepared with ASTM Type II water and 2% HNO_3 (for analysis of all samples).

12.2 All primary standards expire one year after receipt or on the date located on the standard bottle, whichever is earlier.

12.3 All working standards and dilutions of working standards for the ICP that are prepared from primary standards expire 3 months after preparation.

~~12.4 Prepare the 20 ppm working standard ELAN A.~~

12.4.1 Wash a plastic 100 ml volumetric flask with Citranox and hot water. Put 2 ml of concentrated HNO_3 acid into the volumetric and shake. Rinse the volumetric with ASTM Type II water a minimum of three times.

12.4.2 Place about 10 ml ASTM Type II water into the flask.

12.4.3 Pipette 2 ml HNO_3 into the flask and swirl.

12.4.4 Pipette 2 ml of each of the following standards into the flask, swirling after each addition:

Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Ba, Tl, Pb

Always use a new pipette for each standard and never pipette directly out of the primary standard bottle

12.4.5 Dilute the flask to volume with ASTM Type II water and mix well.

12.4.6 Pour the contents of the flask into a clean bottle and label the bottle to describe its contents.

12.4.7 Update the standard log book. Transfer the stock standard number and preparation date from the book to the standard bottle.

12.5 Prepare the 20 ppm standard ELAN B

12.5.1 Wash a 100 ml plastic volumetric with Citranox and hot water. Put 2 ml of concentrated HNO_3 acid into the volumetric and shake. Rinse the volumetric with ASTM Type II water a minimum of three times.

12.5.2 Place about 10 ml ASTM Type II water into the flask.

12.5.3 Pipette 2 ml HNO_3 into the flask and swirl.

12.5.4 Pipette 2 ml each of the 1000 ppm Sb and Mo stock standards into the flask, swirling after each addition. Always use a new pipette for each standard and never pipette directly out of the primary standard source bottle.

12.5.5 Dilute the flask to volume with ASTM Type II water and mix well.

12.5.6 Pour the contents for the flask into a clean bottle and label the bottle to describe its contents.

12.5.7 Update the standard log book. Transfer the stock standard number and preparation date from the book to the standard bottle.

12.6 Prepare the mixed working standards.

12.6.1 Rinse seven 50 ml, and one 100 ml volumetric flasks with ASTM Type II water a minimum of three times.

12.6.2 Place about 20 ml ASTM Type II water into each volumetric flasks.

12.6.3 Each standard should have an acid concentration of 2%. Pipette 1 ml of concentrated nitric acid into each of the 50 ml volumetric flasks, and 2 ml into the 100 ml volumetric flask to achieve this concentration.

12.6.4 Pipette 25 ul of ELAN A solution and 25 ul ELAN B solution into one of the 50 ml volumetric flasks. Dilute to volume with ASTM Type II water and mix. This is a 10 ppb standard.

12.6.5 Pipette 50 ul of ELAN A solution and 50 ul ELAN B solution into one of the remaining 50 ml volumetric flasks. Dilute to volume with ASTM Type II water and mix . This is a 20 ppb standard.

12.6.6 Pipette 125 ul of ELAN A solution and 125 ul of ELAN B solution into one of the remaining 50 ml volumetric flasks. Dilute to volume with ASTM Type II water and mix. This is a 50 ppb standard.

12.6.7 Pipette 250 ul of ELAN A solution and 250 ul of ELAN B solution into one of the remaining 50 ml volumetric flasks. Dilute to volume with ASTM Type II water and mix. This is a 100 ppb standard.

12.6.8 Pipette 40 ul of the 100 ppb standard into the 100 ml volumetric flask. Dilute to volume with ASTM Type II water and mix. This is a 0.04 ppb standard.

12.6.9 Pipette 100 ul of the 100 ppb standard into one of the remaining 50 ml volumetric flasks. Dilute to volume with ASTM Type II water and mix. This is a 0.20 ppb standard.

12.6.10 Pipette 500 ul of the 100 ppb standard into one of the remaining 50 ml volumetric flask. Dilute to volume with ASTM Type II water and mix. This is a 1.0 ppb standard.

12.6.11 Dilute the acid to volume in the final 50 ml volumetric flask with ATSM Type II water and mix. This is a 0 ppb standard.

12.6.12 Update the standard log book. Transfer the stock standard numbers and preparation date to the standard bottles.

12.7 Prepare the Interference Check Solutions (ICS).

12.7.1 The ICSs are prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese.

Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

12.7.2 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

12.7.2.1 Mixed ICS solution I is prepared by weighing into individual weigh boats the following chemicals: 1.39g $Al(NO_3)_3 \cdot 9H_2O$, 0.25g $CaCO_3$ (dried at 180°C for 1 hour before weighing), 0.10g Fe, 1.7g MgO, 0.23g Na_2CO_3, and 0.18g K_2CO_3. These are then added to a 100 ml volumetric flask containing approximately 25 ml of ASTM Type II water. Slowly add 4 ml of (1+1)HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to volume ml with ASTM Type II water.

12.7.2.2 Mixed ICS solution II is prepared by weighing into individual weigh boats the following chemicals: 0.74g 85% H_3PO_4, 0.64g 96% H_2SO_4, 4.0g 37% HCl, and 1.1g citric acid ($C_6O_7H_8$). These are then added to a 100 ml volumetric flask containing approximately 25 ml of ASTM Type II water. Dilute to volume with ASTM Type II water.

12.7.2.3 Mixed ICS solution III is prepared by adding 1.0 ml each of 100 ug/ml arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, silver, and zinc stock solutions to a 100 ml volumetric flask approximately half full of ASTM Type II water. Add 2.0 ml concentrated HNO_3, and dilute to volume with ASTM Type II water.

12.7.2.4 Working ICS Solutions

12.7.2.4.1 ICS-A is prepared by adding to a 100 ml volumetric flask, 10.0 ml of mixed ICS solution I, 5.0 ml of mixed ICS solution II, and 2.0 ml each of 100 ug/ml titanium and molybdenum stock solutions. Dilute to volume with ASTM Type II water and update the standard logbook. ICS-A must be prepared fresh weekly.

12.7.2.4.2 ICS-AB is prepared by adding to a 100 ml volumetric flask, 10.0 ml of mixed ICS solution I, 5.0 ml of mixed ICS solution II, 2.0 ml of mixed ICS solution III, and 2.0 ml each of 100 ug/ml titanium and molybdenum stock solutions. Dilute to volume with ASTM Type II water. Although ICS-AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly. Update the standard log book.

12.7.2.5 The following analytes will be analyzed for in the ICS solutions at the stated concentrations:

ICS-A Working Solution

Element	Concentration (ppm)
Al	100
Mo	20

ICS-AB Working Solution

Element	Concentration (ppm)
Al	100
As	0.02
Cr	0.02
Cu	0.02
Mn	0.02
Mo	2.0
Ni	0.02
Se	0.02
Co	0.02
Ag	0.02
Cd	0.02

13.0 SAMPLE PREPARATION

13.1 Soil, sludge, and waste samples must be digested according to method 3050 prior to analysis. Please see the specific SOP for the detailed preparation procedure.

13.2 Samples that have had an extraction performed on them, such as TCLP, SPLP, EPTox, and ASTM, must first be extracted then be digested using method 3010 or 3015. Please see the specific SOP for the detailed preparation procedure.

13.3 Wastewater samples must be prepared using method 3010 or 3015. Please see the specific SOP for the detailed preparation procedure.

13.4 Oil samples may be digested using method 3051. Please see the specific SOP for the detailed preparation procedure.

13.5 Air samples are prepared using the digestion method specified by the method used in the collection of the samples.

13.6 Pure product samples are prepared according to the manufacturer, or according to a method developed by TriMatrix if available. Please see the specific SOP or dissolution procedure provided by the manufacturer or TriMatrix for the detailed preparation procedure.

13.7 Drinking water samples must have the turbidity checked prior to analysis. Any sample with a turbidity greater than 1 NTU must be digested by method 3015 prior to analysis. Any dissolved sample that has a precipitate must be digested by method 3015 prior to analysis.

14.0 CALIBRATION PROCEDURES

14.1 An initial calibration must be run prior to the analysis of any samples. This initial calibration must be performed daily, or once per every 24 hour analytical batch.

14.1.1 The initial calibration consists of an 8 point standard curve for silver and cadmium, and a minimum of a seven point calibration curve for all other analytes. The initial calibration curve consists of the standards prepared in 12.6. The silver and cadmium curve includes the 0.04 ppb standard. This concentration is not included when processing the curve for the other analytes. The 0 ppb is included as a standard in both curves.

14.1.2 The correlation coefficient must be greater than or equal to 0.995 for every analyte of interest. If the coefficient is less than 0.995, contact the metals lab manager for assistance. All masses that could affect data quality should be monitored to determine potential effects from matrix components on the analyte peak.

14.2 Initial Calibration Verification (ICV).

14.2.1 Immediately following the analysis of the curve, the analysis of an ICV is required. The ICV is a re-analysis of the high level 100 ppb standard prepared in 12.6.7, quantitated as a sample. The acceptance window for this QC is 90% to 110% recovery of the true value. If the ICV is not within the control limits, recalibrate the instrument and start again at step 14.2. If the ICV is still out of the control limits, see the metals lab manager.

14.3 Initial Calibration Blank (ICB)

14.3.1 After the analysis of the ICV, the analysis of an ICB is required. The ICB is a re-analysis of the 0 ppb standard prepared in 12.6.11, quantitated as a sample. The absolute value of the ICB reading must be less than the lowest reporting limit required for the analysis. If the ICB is not within the control limits, recalibrate the instrument and start again at step 14.2. If the ICB is still out of the control limits, see the metals lab manager.

14.4 Interference Check Solutions (ICS).

14.4.1 The interference check solutions were prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The acceptance window for the interference check solution is 80% to 120%. If either one of the interference check solutions are outside of the control windows stop the analysis remake the out of control solution(s) and reanalyze. If the interference check solution(s) are now within the control windows continue the analysis. If either of the

interference check solutions are still out of the control windows stop the analysis, correct the problem, and restart the analysis from the beginning.

14.5 Laboratory Control Sample (LCS).

14.5.1 A LCS must be analyzed to confirm the validity of the curve. The LCS is prepared from a stock dissimilar to that used to prepare initial calibration curve. The control windows for the LCS 90% to 110% recovery of the true values. If the percent recovery does not fall within the control windows, recalibrate the instrument and start the analysis at step 14.2.

14.6 Contract Required Detection Limit (CRDL)

14.6.1 Analyze a CRDL. This is a standard of known concentration at or near the low end of your calibration curve. There is no acceptance criteria for the CRDL other than it must be detected.

14.7 Analyze up to ten samples. A sample is defined as the average of three replicate readings of a solution that is not a standard. The following solutions would qualify as samples: LCSs, MPBs, LFBs, and spiked samples. The only solutions that are not considered samples are the ICV, ICS, ICB, CCB, CCV, and CCB solutions.

14.8 Continuing Calibration Verification (CCV)

14.8.1 Analyze the CCV. The CCV is a standard solution with a concentration of one half the highest standard solution used for the calibration. The acceptance window for this QC is 90% to 110% recovery of the true value. If the CCV is not within the control limits, recalibrate the instrument and start again at step 13.2. All samples since the last good ICV or CCV must be reanalyzed.

14.9 Continuing Calibration Blank (CCB)

14.9.1 Analyze the CCB. The CCB is the calibration blank and has the same acid concentration as the standards. The absolute value of the CCB reading must be less than the lowest reporting limit required for the analysis. If the CCB is not within the control limits, recalibrate the instrument and start again at step 13.2. All samples since the last good ICB or CCB must be reanalyzed.

14.10 Every twelve hours of instrument operation the ICS solutions must be analyzed to verify the magnitude of elemental and molecular ion isobaric interferences and the adequacy of any corrections. The acceptance window for this QC is 80% to 120% recovery of the true value. If the QC is not within the acceptance window for either ICS, stop the analysis, remake the interference check solution and reanalyze. If the QC is now within the acceptance window continue the analysis. If the QC is still outside the acceptance window stop the analysis, correct the problem, and restart the analysis from the beginning.

14.11 Repeat steps 14.7 through 14.9 until the end of the run.

14.12 The analytical batch must end with the analysis of an acceptable CCV and CCB. Again, the acceptance window for the CCV is 90% to 110% recovery of the true value, and the absolute value of the CCB reading must be less than the lowest reporting limit required for the analysis. If either is not within the control limits, recalibrate the instrument and start again at step 14.2. All samples since the last good CCV or CCB must be reanalyzed.

15.0 ANALYTICAL PROCEDURE

NOTE: The following section assumes that the user is familiar with the ELAN 6000 operating software. If you are unfamiliar or unsure, please consult the instrument manual for additional instruction. This procedure will provide adequate instruction for novices, but is not intended to replace the instrument operating manual.

15.1 Preliminary treatment of all matrices is always necessary because of the complexity of variability of sample matrices. Digestion procedures are presented in sample preparation methods (method 3005-3050/200.0/200.7). A minimum of five internal standards is always used.

15.2 Turn on the instrument.

15.2.1 Turn on the main power if it is not already on.

15.2.2 Turn on the Rf generator power if it is not already on.

15.2.3 Turn on the autosampler power if it is not already on.

15.2.4 Turn on the recirculator power if it is not already on.

15.2.5 Turn on the Ar gas supply if it is not already on.

15.2.6 Turn on the hood above the instrument if it is not already on.

15.3 Boot the computer and ELAN 6000 software.

15.3.1 If the computer is already on the ELAN software is running, skip to step 14.4. If you are unsure of the status of the computer, please see the metals manager.

15.3.2 Turn on the computer, monitor, and printer. If any of the devices fail to turn on, please see the metals manager.

15.3.3 When the computer boots, it will display:
Welcome
Press Ctrl + Alt + Del to log on.

15.3.4 The screen will display:
Welcome
username: Elan user
from: ICP-MS
password: ____
Just press enter do not enter anything as a password.

15.3.5 The screen will display:
Program manager and Elan 6000 (common)
move the arrow to Elan and click on it

15.3.6 The screen will display:
a general Elan 6000 window
move arrow to devices and click on it. This will bring up the pump page.

15.4 Change the peristaltic pump tubing. Currently, three types of tubing are being used:

Black/Black	Sample line
Orange/Green	Internal standard line
Black/White	Waste line

The tubing should be changed for every run since the tension exerted on the tubing by the pump will cause the tubing to stretch. Place the waste line on the bottom so that the pump is pumping the waste away from the ICP. Place the internal standard line in the middle so that the pump is pumping the internal standard toward the ICP. Place the sample line on the top so that the pump is pushing the sample to the ICP. Update the instrument maintenance log to reflect that you change the pump tubing.

15.5 Click on the connect icon box then click on the ---> icon box this should turn the pump on in a counterclockwise direction. If the pump does not turn on. Click on the disconnect icon. Then click on the connect icon. Then click on the ---> icon and the pump should be turning in the counterclockwise direction. If the pump still is not on contact the metals lab manager.

15.6 Move the arrow to the instrument icon and click on it. There should be a picture of the ICP-MS and some of its components on the screen if there is not click on the front panel icon.

15.6.1 On the picture of the ICP-MS. There should be a number of components that are green and the status box should say Ready. Consult the instrument manual as to which components should be green.

15.6.2 If the status is Ready, move the arrow to the plasma icon box and click on start. The instrument will display an ignition icon bar until it has achieved a good plasma.

15.7 Once the plasma has been on for at least one half hour daily tuning of the instrument needs to be done.

15.7.1 Move the arrow to File. Highlight open workspace then click on x,y.wrk. This will align the plasma to the best spot on the sampler and skimmer cones. Place the sample tubing into a 10 ppb tuning solution of Rhodium, Lead, and Magnesium. Click on Analyze Sample and adjust

the x,y knobs to get the highest Rhodium reading. This is typically 250,000 cps to 300,000 cps.

15.7.2 Next you will need to optimize the nebulizer flow and lens voltage. Move the arrow to File and highlight NLP.wrk. Place the sample line in the 10 ppb tuning solution and make sure that nebulizer flow is highlighted. Click on Analyze Sample. The computer will automatically adjust the nebulizer flow between 0.4 and 0.7 L/min. This range can be changed but has been found to be the best. When the instrument is finished go to File and click on Save.

15.7.3 Next highlight Lens Voltage and click on Analyze Sample. The computer will automatically pick the best lens voltage for you. The value is typically from 4 to 6 if it is not fix the problem and start the tuning procedure form 14.7.1. When the instrument is finished go to File and click on Save.

15.7.4 Next you will need to tune the mass spec. over the whole mass range. Go to File click on Open workspace. Click on TriMatrix Int.wrk. Place the internal standard line into the mixed internal standard bottle. Click on Tune Mass Spec. You want to get a value of 0.65 amu or less at 10% peak height. This has been shown by the instrument manufacturer to equal 1 amu peak width at 5% peak height. If the required resolution was not achieved. Manually adjust the DAC and try again, generally increasing it by 30 will decrease the Amu reading by 0.1. When the desired Amu reading has been achieved for all the referenced analytes then go to File and click on Save.

15.7.5 Next do a daily performance to see how the instrument is operating. Go to File and click on Daily.wrk. Place the sample probe into the 10 ppb tuning solution and click on Analyze Sample. The instrument will take a reading of certain masses and doubly charged ions and oxides. All % RSDs should be less than 5% if not repeat the procedure once. If it is in the limits go to 14.7.6. If not stop the tuning procedure. Correct the problem and begin again for 14.7.1.

15.7.6 Next you will need to optimize the ion lens over the full mass range. Go to File and click on Open Workspace. Then Lens Optimization. Put the internal standard lime into the mixed internal standard bottle. Click on Clear Calibration. Then get analyte list, click on Optimize. The computer will automatically adjust the voltage to the ion lens finding the maximum value for each internal standard. When the optimization is done go to File and click on Save.

15.7.7 Once all of the optimization steps are complete you are ready to calibrate and run samples.

15.8 The table below lists the element conditions in use at the time of this writing. Please note that any or all of the conditions listed below may change for an element without prior warning if it has been established that the new conditions are at least equivalent to those in the table.

Int Std	Analyte	Mass [amu]	Scan Mode	MCA Channels	Dwell Time per AMU [ms]	Integration Time [ms]	Corrections
Li		6.0151	Peak Hopping	1	100	1000	
	Be	9.0122	Peak Hopping	1	100	1000	
Sc		44.9559	Peak Hopping	1	100	1000	
	V	50.944	Peak Hopping	1	100	1000	C10, Cr
	Cr	52.9407	Peak Hopping	1	100	1000	
	Mn	51.9405	Peak Hopping	1	100	1000	
	Co	58.9332	Peak Hopping	1	100	1000	
	+Ni	59.9332	Peak Hopping	1	100	1000	
	Ni	60.931	Peak Hopping	1	100	1000	
	+Cu	62.9298	Peak Hopping	1	100	1000	
	Cu	64.9278	Peak Hopping	1	100	1000	
	+Zn	65.926	Peak Hopping	1	100	1000	
	Zn	66.9271	Peak Hopping	1	100	1000	
	Zn	67.9249	Peak Hopping	1	100	1000	
	As	74.9216	Peak Hopping	1	100	1000	ArCl, Se
	Se	81.9767	Peak Hopping	1	100	1000	
Ge		88.9054	Peak Hopping	1	100	1000	
	Mo	97.9055	Peak Hopping	1	100	1000	Ru
	+Ag	106.905	Peak Hopping	1	100	1000	
	Ag	108.905	Peak Hopping	1	100	1000	
	+Cd	110.904	Peak Hopping	1	100	1000	Mo, Pd
	Cd	113.904	Peak Hopping	1	100	1000	Sn
In		114.904	Peak Hopping	1	100	1000	Sn
	Sb	120.904	Peak Hopping	1	100	1000	
	+Sb	122.904	Peak Hopping	1	100	1000	Te
	Ba	134.906	Peak Hopping	1	100	1000	
	+Ba	136.905	Peak Hopping	1	100	1000	
Tb		158.925	Peak Hopping	1	100	1000	
	Tl	202.972	Peak Hopping	1	100	1000	
	+Tl	204.975	Peak Hopping	1	100	1000	
	Pb	207.977	Peak Hopping	1	100	1000	Pb, Pb
Bi		208.980	Peak Hopping	1	100	1000	
*	Br	208.980	Peak Hopping	1	0.1	1	
*	Cl	34.9689	Peak Hopping	1	0.1	1	
*	Ca	43.9555	Peak Hopping	1	0.1	1	
*	Mg	23.985	Peak Hopping	1	0.1	1	
*	Na	22.9898	Peak Hopping	1	0.1	1	
*	Fe	56.9354	Peak Hopping	1	0.1	1	
*	K	38.9637	Peak Hopping	1	0.1	1	
*	Ar Cl	76.9283	Peak Hopping	1	0.1	1	
*	Kr	82.9141	Peak Hopping	1	0.1	1	
*	Ru	100.906	Peak Hopping	1	0.1	1	
*	Pd	105.903	Peak Hopping	1	0.1	1	
*	Mo^{O}	107.901	Peak Hopping	1	0.1	1	
*	Sn	117.902	Peak Hopping	1	0.1	1	
*	Te	124.904	Peak Hopping	1	0.1	1	

* Used for reference purposes only
\+ Recommended Analytical Mass

Approved By: 11/23/98 QA Manager
Approved By: 11/23/98 Area Manager

15.8.1 The Table below lists the elemental equations being used at this time. Please note that any or all of these equations may change without prior warning if it has been established that the new equations are at least equivalent to those below:

Analyte	Equation
Al	$(1.00)(^{27}C)$
Sb	$(1.00)(^{123}C)$
Sb	$(1.00)(^{121}C)$
As	$(1.00)(^{75}C)-(3.127)[(^{77}C)-(0.815)(^{82}C)$
Ba	$(1.00)(^{137}C)$
Ba	$(1.00)(^{135}C)$
Be	$(1.00)(^{9}C)$
Cd	$(1.00)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$
Cd	$(1.00)(^{114}C)$
Cr	$(1.00)(^{52}C)$
Cr	$(1.00)(C)$
Co	$(1.00)(^{59}C)$
Cu	$(1.00)(^{63}C)$

15.9 Set up the analysis on paper using a sample identification weight sheet (ID/WT sheet). This sheet has columns where the operator enters the sample description, corresponding autosampler position number, digestion dilution (if any), and any subsequent dilutions performed on the sample. This sheet must be filled out before continuing with the procedure as it is an integral part of the analysis. Please see the group leader or metals lab manager if assistance is required in filling out this sheet.

15.9.1 Enter the method by moving the arrow to File and clicking on it. Then click on open workspace you will have a number of choices, but only choose between 200.8 Trimatrix.wrk, and Trimatrix soil.wrk.

15.9.2 Open a new data set. To do this move the arrow to the data set icon and click on it. Then move the arrow to file and click on it and choose new. You will need to enter a unique data file name. The current data file format is MDDAAAA-X,
where:
M = coded month
DD = two digit date of the month
AAAA = matrix that is running (i.e. soil, wtr, TCLP, WW)
X = Alpha representation of the number of runs that have been done under that matrix for that day (i.e. the first run would be 'a', the 5th run would be 'e').

15.9.3 Enter the sample list as identified on the ID/WT sheet. Please refer to the ELAN 6000 software manual for data entry procedures. When all the information is entered you will need to save the sample file. To do this go to file and click on save as. Use the same data file name here as you used for the data set.

15.10 Begin the analysis.

15.10.1 Make sure that batch is highlighted . Highlight the samples that you want to run and click on the analyze batch icon.

15.10.2 The computer will ask you a series of yes and no questions. If you are starting a new run answer yes to all of the questions. Then the computer will start the run.

15.10.3 A measurement status box will be displayed on the screen at this time. It will tell you what the instrument is doing. It will also give you three options to stop a run at any time click on canal. To stop after the current sample click on stop scanning after current sample, or to skip the sample click on skip scanning of current sample.

15.10.4 If you have stopped a run for any reason and want to continue the analysis from where you left off go to 14.6.1.

15.11 When the analysis is completed, the autosampler will return to position 0 and wait for operator input.

15.12 Turn the raw data, ID/WT sheet, and report to the person who is to review the data for repeats, dilutions, etc.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The concentration of each sample is read directly from the computer printout. Dilution factors should be taken into account in the ID weight file.

16.1.1 Assuming that the instrument did not correct a concentration due to analyst error, the following calculation would be used:

$C_{Final} = C_{Instr} * DF_{Digest} * DF_{Subseq}$,, where:

C_{Final} = final reported concentration of the analyte
C_{Instr} = concentration as read from the instrument data printout
DF_{Digest} = digestion dilution factor
DF_{Subseq} = dilution due subsequent to the digestion dilution

16.2 All samples should be reported to the correct number of significant figures. The significant figure truncation should not be performed until all data calculation have taken place.

16.2.1 Solid samples must be reported in mg/kg.

16.2.1.1 For sample concentrations <100 ppm, report 2 significant figures.

16.2.1.2 For sample concentrations ≥ 100 ppm, report 3 significant figures.

16.2.1.3 For QC always report one additional significant figure.

16.2.2 Aqueous samples must be reported in ug/L.

16.2.2.1 For sample concentrations < 10 ppb, report 1 significant figure.

16.2.2.2 For sample concentrations ≥ 10 ppb and < 1000 ppb, report 2 significant figures.

16.2.2.3 For sample concentrations ≥ 1000 ppb, report 3 significant figures.

16.2.2.4 For QC always report one additional significant figure.

16.2.3 Extracted samples for all metals must be reported in mg/L.

16.2.3.1 For sample concentrations <0.01 ppm, report 1 significant figure.

16.2.3.2 For sample concentrations ≥ 0.01 ppm and <1.00 ppm, report 2 significant figures.

16.2.3.3 For sample concentrations ≥ 1.00 ppm, report 3 significant figures.

16.2.3.4 For QC always report one additional significant figure.

17.0 DATA REPORTING AND DELIVERABLES

17.1 See appendices F, H, I, and J for data reporting.

18.0 QUALITY ASSURANCE

18.1 All quality control data should be maintained and available for easy reference or inspection.

18.2 Linear range studies must be performed every year or when there is a significant change in the instrument response.

18.2.1 To perform a linear range study, calibrate the instrument as it would be calibrated for an actual analysis.

18.2.2 Run standards at high concentrations and calculate the percent recovery for each element. A good place to start is 1 ppm.

18.2.3 If the percent recovery is acceptable (90%-110%), run a standard at a higher concentration. If the percent recovery is not acceptable, run a standard at a lower concentration.

18.2.4 The last standard concentration that had a percent recovery within the acceptance window will be designated as the linear range for that element.

18.3 IDL/MDL studies must be performed on an annual basis.

18.3.1 Instrument Detection Limits (IDLs) in ug/L can be estimated by calculating the average of the standard deviation of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples).

18.3.2 To calculate an MDL, aspirate ten vials of a low concentration standard, typically at a concentration at or near the detection limit. Calculate the standard deviation of a small population and multiply the result by the Student's T value for (n-1) degrees of freedom. If the concentration of the standard ran is greater than ten times the calculated MDL, and the concentration of the standard ran is above the detection limit reported to clients, the MDL must be performed at lower concentration. If the standard concentration is less than ten times the calculated MDL or if the standard used for the analysis was at or below the lowest reporting limit on LIMS, the MDL is acceptable. There is also a spreadsheet located on the computer network that will perform this calculation for you. Please see the metals lab manager if you need assistance in using this program.

18.4 Dilute and reanalyze samples that are more concentrated than the established linear range.

18.5 Include a minimum of one laboratory blank per sample batch to determine if contamination or any memory effects are occurring. This laboratory blank must be carried through the sample preparation procedure.

18.6 Analyze one matrix spike (MS) and one matrix spike duplicate (MSD) at a frequency of at least 1 in 20 (5%). MS and MSDs are aliquots of sample into which a known quantity of analyte is pipetted in. The percent recovery of the analyte is calculated. This measures the accuracy of the sample preparation method as well as the effect of the matrix on the analysis. The relative percent difference is calculated from the MS and MSD concentrations. The MSD checks the precision of the method. The percent recoveries should be between 70 percent and 130 percent of the spiked value.

18.6.1 Pretreated samples must be spiked at the time of digestion before the digestion has begun. Please see the specific pretreatment procedure for a discussion on spiking procedures.

18.6.2 Samples that require dilutions that have an MS/MSD performed on them must also have an MS/MSD performed on an aliquot of dilution.

18.6.3 Samples not requiring pretreatment are spiked before they are physically loaded on the tray.

18.6.3.1 See Appendix A for the method used to spike samples.

18.6.3.2 If the method in Appendix A is followed when spiking you should get 40 ug/L as a final concentration.

18.6.4 Calculate the percent recovery of the MS and MSD as follows,

$$\%R = \frac{C_{Spike} - C_{Orig}}{\text{Spike Quantity}} * 100,$$

where:

%R = percent recovery of the spike
C_{Spike} = concentration of the spiked sample
C_{Orig} = original concentration of the sample (the unspiked sample concentration)
Spike Quantity = quantity of the element spiked into the sample

18.6.5 Calculate the relative percent difference between the MS and MSD as follows:

$$\%RPD = \frac{C_{MSD} - C_{MS}}{(C_{MSD} + C_{MS})/2} * 100$$

where:

%RPD = relative percent difference between the MS and MSD
C_{MSD} = concentration of the MSD as read from the raw data printout
C_{MS} = concentration of the MS as read from the raw data printout

18.7 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 18.7.1 through 18.7.3, will ensure the analyst that neither positive nor negative interferences are operating on any of the analytes to distort the accuracy of the reported values.

18.7.1 **Serial dilution**: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrument detection limit after dilution), an analysis of 5X dilution must agree within 10% of the original determination. If not, a chemical physical interference effect should be suspected. And standard addition must be performed.

18.7.2 **Matrix spike addition**: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered within 75% to 125% of the known value. The spike addition should produce a minor level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specific limit, matrix effect should be suspected. The use of a standard-addition analysis procedure can usually compensate for this effect.

18.7.3 **Standard addition**: The standard-addition technique involves adding known amounts of standard to one or more aliquots of the process sample solution. This technique compensates for a sample constitute that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct additive interferences which

could a baseline shift. The simple version of this technique is the single addition method, in which identical aliquots of the sample solution, each of volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_X is calculated:

$$C_X = \frac{S_B * V_S * C_S}{(S_A - S_B) * V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is must greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration;

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. the signal must be corrected for any additive interference.

The intensity of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

NOTE: A method of standard addition must be performed on any TCLP sample whose spike recovery is not greater than 50%.

18.8 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

NOTE: Steps 18.8.2 through 18.8.6 must be performed every time the instrument is calibrated.

18.8.1 Calibrate the instrument using a standard and a blank.

18.8.2 An ICS/ICV (Initial Calibration Standard/Initial Calibration Verification) is placed after the calibration standards and blank. Percent recovery limits are 90% to 110% of the original calibration standard concentration. If the percent recovery for this standard is not within the acceptance limits for an element that must be analyzed, terminate the analysis, correct the problem, recalibrate, and restart the analysis.

18.8.3 An ICB/CCB (Initial Calibration Blank/continuing Calibration Blank) is analyzed after the ICV. The results of this blank are to be within ± the detection limit. If the blank is not within

± the detection limit for an element that must be analyzed, terminate the analysis, correct the problem, and restart the analysis from the beginning.

18.8.4 The interference check solutions is analyzed at the beginning and end of each run and every 12 hours of instrument operation. This standard is analyzed to demonstrate the magnitude of interferences and provide an adequate test of any corrections. Percent recovery limits are 80% to 120% of the actual concentration. If the percent recovery for this standard is not within acceptance limits. Stop the run remake the standard and reanalyze. If it is now within limits continue the analysis stop the run remake the standard and reanalyze. If it is now within limits continue the analysis. If the standard is still outside of the acceptance limits stop the run, correct the problem, and restart the analysis from the beginning.

18.8.5 An LCS (Laboratory Check Standard), which must come from a different primary source than the calibration standards, is placed after the first CCV in each run. Percent recovery limits are 80% to 120% of the concentration unless control limits have been established. If the percent recovery for this standard is not within the acceptance limits for an element that must be analyzed, terminate the analysis, correct the problem, recalibrate, and restart the analysis from the beginning. See the following table for a tabulation of the LCS concentrations as of this writing. Dashes in the table indicate that the element to the left is not present in the solution.

LCS Concentration When Diluted According to Instructions

Element	SP1036 (ug/L)	SP1037 (ug/L)	ERA 9965
Aluminum	80	---	59.3
Antimony	---	80	11.1
Arsenic	80	---	5.19
Barium	80	---	29.6
Beryllium	80	---	8.89
Cadmium	80	---	8.15
Chromium	80	---	23.0
Cobalt	80	---	55.6
Copper	80	---	44.8
Lead	80	---	43.0
Manganese	80	---	16.3
Molybdenum	---	80	20.7
Nickel	80	---	31.9
Selenium	80	---	17.8
Silver	80	---	8.89
Thallium	80	---	5.19
Vanadium	80	---	11.7
Zinc	80	---	47.4

18.8.6 Verify the calibration after every 10 samples.

18.8.6.1 A CCV (Continuing Calibration Verification) is analyzed after every 10 samples, or sooner. Percent recovery limits are 90% to ~~110~~% of the concentration. If the

110 [illegible]

percent recovery for this standard is not within the acceptance limits for an element that must be analyzed, terminate the analysis, correct the problem, recalibrate, and restart the analysis from the last good CCV or ICS/ICV.

18.8.6.2 A CCB (Continuing Calibration Blank) is analyzed after the CCV. The results of this blank are to be within ± the detection limit. If the blank is not within ± the detection limit for an element that must be analyzed, terminate the analysis, correct the problem, recalibrate, and restart the analysis from the last good CCB or ICB/CCB.

18.8.7 At the end of each run, verify the calibration.

18.8.7.1 A CCV (Continuing Calibration Verification) is analyzed at the end of each run. Percent recovery limits are 90% to 110% of the concentration. If the percent recovery for this standard is not within the acceptance limits for an element that must be analyzed, terminate the analysis, correct the problem, recalibrate, and restart the analysis from the last good CCV or ICS/ICV.

18.8.7.2 A CCB (Continuing Calibration Blank) is analyzed after the CCV. The results of this blank are to be within ± the detection limit. If the blank is not within ± the detection limit for an element that must be analyzed, terminate the analysis, correct the problem, recalibrate, and restart the analysis from the last good CCB or ICB/CCB.

18.8.7.3 An interference check solution is analyzed at the end of the run. This standard is analyzed to demonstrate the magnitude of interferences and to provide an adequate test of any collections. Percent recovery limits are 80% to 120%. If the percent recovery is not within acceptance limits. Stop the run, remake the standard, and reanalyze. If it is now within limits continue the analysis. If it is still outside of the acceptance limits, stop the run, correct the problem, and restart the analysis from the beginning.

18.9 Internal standardization must be used in all analysis to correct for instrument drift and physical interferences. A minimum of five internal standards are used at all times. For any sample that is to be run by method 200.8, the recovery requirement for each internal standard is 60-125% of the true value. For any sample analyzed by method 6020, the recovery limits are 30-120%.

18.9.1 If the internal standard recovery is low, the sample must be diluted 1:5 and reanalyzed. If the internal standard recovery is still low, a further 1:5 dilution is required. This process is repeated until satisfactory recoveries are achieved.

18.9.2 If the internal standard recovery is high, then the internal standard compound may naturally be present in the sample, and a different internal standard must be used.

19.0 ANALYST CERTIFICATION/METHOD VALIDATION

19.1 Please see section 3.8.3 and 3.9.3.2 of the TriMatrix Quality Assurance Manual and Appendix E for analyst and method certification/validation protocols.

20.0 REFERENCES

20.1 ELAN 6000 Software Guide; Perkin Elmer Corporation; Manual 0993-8965, Release E, June 1995.

20.2 ELAN 6000 Hardware Guide; Perkin Elmer Corporation; Manual 0993-8969, Release D; September 1995.

21.0 ATTACHMENTS/APPENDICES

21.0 See Attached

Approved By: 11/23/98 QA Manager

Approved By: 11/23/98 Area Manager

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

MERCURY ATOMIC ABSORPTION FOR THE ANALYSIS OF LIQUID WASTE: AUTOMATED COLD VAPOR TECHNIQUE

MODIFIED METHODS 7470 and 245.1

UNCONTROLLED DOCUMENT

APPROVALS:

Inorganic Manager: _____ Date: 12/4/98
Douglas E. Kriscunas

QA Manager: _____ Date: 12/4/98
Rick D. Wilburn

Laboratory Manager: _____ Date: 12/4/98
Douglas E. Kriscunas

Procedure Number: GR-01-123
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Pages Revised: All

By: Dave Johnson

Total Number of Pages: 32

1.0 SCOPE AND APPLICATION

1.1 Method 7470/245.1 is a combination of USEPA Methods 7470, 245.1. This method may be used for the determination of total mercury (inorganic and organic) in mobility-procedure extracts, aqueous wastes, ground waters, drinking waters, surface waters, saline waters, domestic and industrial wastes. All samples analyzed by this method must undergo a procedure to destroy any organic substances in the sample prior to analysis.

2.0 PRINCIPAL METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, September, 1994, Method 7470A, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)".

2.2 *Methods for the Determination of Metals in Environmental Samples,* Supplement I, May 1994, Revision 5.4, EMMC Version, "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry", Method 245.1, Revision 3.0, May, 1994.

3.0 SUMMARY OF PROCEDURE

3.1 Prior to analysis, all samples, standards, and quality control samples must be prepared according to the procedure discussed in Section 12 of this method. This digestion procedure breaks down organo-mercury compounds into inorganic mercury. The inorganic mercury is then converted to the Hg^{+2} state for subsequent analysis

3.2 The prepared liquid sample with mercury in the divalent form (Hg^{+2}) enters the mercury analysis system and is mixed with stannous sulfate to form elemental mercury vapor (Hg^0) according to the following equation:

$$Hg^{+2} + Sn^{+2} \text{-------}> Hg^0 + Sn^{+4}$$

3.3 The mixture flows into a liquid-gas separator where argon is introduced to carry the mercury through a drying tube containing magnesium perchlorate. The dry mercury vapor then enters one path of a heated double-path optical cell that has been optimized for fast response time. A mercury source powered by a constant current power supply delivers a stable source of emission at 253.7 nm. Absorbance by the mercury vapor is measured using a solid state detector with a wide dynamic range. The resulting signal is referenced to the simultaneous absorbance of the pure carrier gas flowing through the second optical path under identical conditions. The absorbances of the standards are plotted against the known concentration. Absorbance readings from unknown samples are then read from the standard curve and extrapolated to the concentration. The mercury vapor is then captured on activated carbon and the argon is vented up a hood to reduce the potential for contamination of other samples.

3.4 This SOP describes the current procedure that is in use at TriMatrix. Since this method uses the Leeman AP200 and PS200 to analyze aqueous samples, the following modifications have been implemented. The

amount of sample to be digested has been reduced from 100 ml to 8 ml due to sample vial size. All of the reagents in the method have been scaled back proportionally to the new sample volume of 8 ml. The new 245.1 method does not require that the standards be digested, but method 7470 still requires that the standards be digested. Since TriMatrix still digests all standards and quality control checks, TriMatrix will continue to use the control limits established in Method 7470 and the older 245.1 methods. The digestion of samples is accomplished in the Leeman AP200 digestion unit that adds all reagents, cooks the samples, reduces the samples, and purges the samples with argon. The analysis of samples utilizes the Leeman PS200 system that is a dedicated mercury analysis system. The PS200 is a flow-through system that reduces the mercury to the ground state, then sweeps the vapor into a heated flow cell.

3.5 The typical reporting limit for this method is 0.2 µg/L. The instrument detection limit for this procedure is 0.174 µg/L.

4.0 PARAMETER OR COMPOUND LIST

4.1 Mercury

5.0 REFERENCED SOPs

5.1 None referenced.

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Soil samples often contain mercury at low levels. When soils are mixed and ground, there exists the possibility that the liquid samples may become contaminated. Therefore, the preparation area for mercury must be kept free of dust and dirt to avoid contamination.

6.2 Certain volatile organic materials that absorb at this wavelength (253.7 nm) may also cause interference. If an interference is suspected, a preliminary run without reagents should determine if this type of interference is present.

6.3 The headspace at the top of the vial must be purged with argon prior to analysis. This step will sweep any chlorine away from the sample to reduce the potential from the chlorine interference.

6.4 The non-metals lab uses a product called Chrome-merge that contains mercury at fairly high concentrations to clean BOD bottles. Since some of the glassware used in this procedure is cleaned in the same area as the BOD bottles, care should be taken to minimize the potential of contamination from this source. If the glassware has become contaminated with the reagent, all suspected glassware must be thoroughly washed again prior to use.

6.5 If a mercury thermometer is broken anywhere in the laboratory, the metals lab will be notified. There always exists the possibility that sample vials may become contaminated from the mercury vapor from the broken thermometer. If contamination is suspected, the vials must be dumped and the samples redigested.

6.6 Mercury may be lost if the temperature of the water bath used to perform the digestion goes above 95°C. All water baths used for digestion must have their temperature monitored with an alcohol thermometer. The temperature of the water bath must be recorded in the mercury digestion logbook.

6.7 The reagents used in this procedure may become contaminated over time. If contamination is suspected, the reagent must be discarded and fresh reagent made.

7.0 SAFETY PRECAUTIONS

7.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the TriMatrix Laboratory Safety Manual.

7.2 Concentrated acids are used in the preparation of standards and samples for analysis by cold vapor. Gloves and safety glasses must be worn at all times when handling concentrated acids. Gloves must also be worn when handling digested samples. Please refer to the MSDS for information on these or any other chemicals utilized in this procedure.

7.3 Check the exhaust hood over the instrument to be sure it is operating correctly. If the ventilation system is not working properly, immediately contact the metals lab supervisor. Under no circumstances should the cold vapor unit be used if the exhaust hood is not working.

7.4 UV protective glasses must be worn at all times in the metals laboratory. The mercury lamp emits UV radiation. Avoid looking directly at the lamp without some type of strong UV protection. Failure to follow this policy may cause very serious and immediate damage to the retina of the eye.

7.5 The cold vapor unit and the mercury digestion units use gaseous Ar. Although Ar in and of itself is not hazardous or flammable, it may cause suffocation through oxygen deprivation. It is therefore imperative that all sources of Ar be turned off with a valve when not in use. Since Ar is colorless and odorless, if you feel lightheaded, please evacuate the metals lab at once and notify the metals lab supervisor. Please refer to the MSDS for information on this or any other chemicals utilized in this procedure.

7.6 Mercury exists in many forms, and is toxic in a variety of ways. Mercury vapor is toxic if inhaled. Do not operate the instrument if it is not properly ventilated. Hg^{+2} is toxic if ingested. Always wash hands after handling the mercury standard.

7.7 No food or drink is allowed in the metals lab. Food or drink may become contaminated with acid or metals and may therefore be hazardous.

7.8 Wash hands before starting work. Chemicals may be present on the skin that may interfere with metals analysis. Wash hands before leaving the metals lab. Chemicals and acids may be on the skin that could eventually be ingested or passed on to a third party through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 All sample containers must be pre-washed with detergents, acids and ASTM Type II water. Plastic and glass containers are both suitable, although glass is preferable since mercury may be adsorbed by certain plastics.

8.2 Aqueous samples must be preserved at the time of collection to pH <2 with HNO_3. The suggested maximum holding time for aqueous samples for mercury analysis is 28 days.

8.3 All samples and standards must be subjected to the digestion that is detailed in Section 12.

8.4 The minimum samples size for this test is 25 ml. If quality control is to be performed on the sample, 75 ml is the minimum sample volume required.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Laboratory analytical balance capable of weighing 0.1 mg.

9.2 Laboratory balance capable of weighing 0.1 g.

9.3 Eppendorf pipettors capable of delivering 50-1000 µl.

9.4 Class A volumetric flasks, various volumes.

9.5 Class A reusable pipettes, various volumes.

9.6 Oxford pipettes capable of 5 to 10 ml of solution.

9.7 Magnetic stir plate and stir bar.

9.8 Laboratory spatulas. The spatulas must be cleaned prior to use.

9.9 Glass alcohol thermometer. Mercury thermometers must never be used in this procedure. The thermometer must be able to reach 95°C.

9.10 15 ml sample vials, glass. The vials must be capable of fitting in the AP200 autosampler rack. Currently, all of the glass vials are blown specifically for use with the AP200 unit. If the vials are weak in any way, they will crack when subjected to the preparation procedure. Do not use vials that are cracked at the top since excess evaporation may occur during digestion.

9.11 Leeman Labs AP200 automated mercury preparation system. The computer-controlled instrument dispenses reagents to each mercury sample in accordance with methods 245.1 and 7470. The unit then heats the samples to 95°C in a water bath for 2 hours. The samples are then cooled and the excess permanganate is reduced by the instrument. After the samples have been purged with Ar gas, the samples are ready for analysis using the PS200.

9.12 Computer running Leeman AP 200 control software. An IBM compatible 80386SX16 or better computer with at least 1 MB RAM, a 40 MB hard disk, and a VGA color monitor is needed. The current software used by the instrument is AP200 version 2.043. The software version may be updated without notice if it performs at least as well as the older version. Major updates to the software that require the analyst to deviate from the stated procedure will require an update to this SOP.

9.13 Leeman Labs PS200 automated mercury system. The instrument has an attached autosampler that is capable of aspirating sample and reagents. A regulator is built into the instrument to deliver the Ar to the sample stream. The instrument is a double-beam instrument capable of measuring the change in intensity of a mercury lamp at 253.7 nm. The Ar used to purge the mercury vapor from the sample is used as the reference beam. To compensate for any aberrations in the optical path, the instrument has an adjustment screw to tune the path so that they react the same to the emission of the mercury lamp.

9.14 Computer running Leeman PS 200 control software. An IBM compatible 80386SX16 or better computer with at least 1 MB RAM, a 40 MB hard disk, and a VGA color monitor is needed. The current software used by the instrument is PS200 version 2.008. The software version may be updated without notice if it performs at least as well as the older version. Major updates to the software that require the analyst to deviate from the stated procedure will require an update to this SOP.

9.15 Epson printer or equivalent. The specific printer used must respond to Epson printing codes. The printer must be attached to the computer using an appropriate communication cable. Please refer to the Instrument manual for further printer specifications.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Check calibration on pipettors prior to use. Please refer to the Eppendorf pipettor SOP for calibration procedures and corrective actions.

10.2 Verify calibration of the balance. Please refer to the balance SOP for calibration procedures and corrective actions.

10.3 Inspect the Ar supply when the shift begins. If the liquid level of the Ar falls below the reorder mark, notify the person responsible for ordering gasses or the metals lab supervisor.

10.4 Inspect the waste container on the floor by the instrument every shift. If the jug is full, properly dispose of the liquid.

10.5 The reagent valves on the AP200 must be checked and replaced periodically. Inspect all of the reagent valves prior to use. If the valve appears to be leaking, replace the valve. Please refer to the AP200 users manual for instructions on changing the reagent valve. Note the replacement in the instrument maintenance logbook.

10.6 Since the AP200 operates in a very corrosive atmosphere, the autosampler needs periodic maintenance.

10.6.1 Prior to the start of each batch of samples, the following steps should be performed.

10.6.1.1 Wet the rails with isopropyl alcohol.

10.6.1.2 Move the tip assembly back and forth slowly along the rails to pick up the alcohol.

10.6.1.3 Wipe the rails dry with a clean soft cloth.

10.6.1.4 Place two drops of light machine oil on both rails.

10.6.1.5 Move the tip assembly back and forth slowly along the rails to pick up the oil.

10.6.1.6 Wipe the rails lightly to remove any excess oil.

10.6.1.7 Note the maintenance in the instrument maintenance logbook.

10.6.2 If the autosampler has been exposed to concentrated acid or if the autosampler jams during a digestion batch, perform the following steps.

10.6.2.1 Wet the rails and the entire tip assembly with water to dilute the acid and decontaminate all exposed surfaces.

10.6.2.2 Move the tip assembly back and forth slowly along the rails to get water into the bearings

10.6.2.3 Repeat Steps 9.6.2.1 through 9.6.2.2 until all of the acid has been removed from the assembly.

10.6.2.4 Perform Steps 9.6.1.1 through 9.6.1.7

10.7 Inspect the autosampler probe on the AP200 prior to each use. The probe should not be bent and should be able to enter each of the sample vials without obstruction. If the probe is bent, replace it with a new one. Note the change in the instrument maintenance logbook.

10.8 Inspect the printing quality of the printer. If the print is hard to read or light in appearance, replace the printer cartridge with the appropriate replacement.

10.9 Check all tubing on the PS200 for flattened areas, leaks, and clogs before use. If any problems are found, change the tubing and note the change in the instrument maintenance logbook.

10.10 Prior to analysis, rinse the entire PS200 system with 1:3 HCl for about ½ hour followed by ASTM Type II H_2O for another ½ hour.

10.11 The aperture on the PS200 must be checked before the analysis has begun. See the analytical method for a discussion on how the aperture is tested.

10.12 The PS200 instrument must be given the appropriate amount of time to warm up before use. If the instrument has been shut down in 'Overnight' mode, it is highly recommended that the 'WARMSTRT' macro be invoked to warm the instrument up. If the instrument has been shut down for an extended period of time, the 'COLDSTRT' macro should be used.

10.12.1 The WARMSTRT macro asks a series of questions to the user to ensure that everything is in place and is in working order. The instrument then warms up for 20 minutes to condition the tubing and stabilize the lamp. While answering the questions, if the user enters an invalid response, the macro will not continue. For example, one of the questions is 'Is the lamp on? <Y/N>'. If the user enters anything but 'Y', the macro will not continue. When the macro has completed the warm-up period, the message 'System Ready' is displayed on the screen. If the macro was called from another macro, such as the MERCURY macro, then control is given back to the calling macro and the calling macro will resume at the step after the call to the macro.

10.12.2 The COLDSTRT macro is similar to the WARMSTRT macro, but the warm-up period is much longer since it will be invoked only if the instrument has been shut down for an extended period of time. Again, the questions are programmed such that only certain responses will allow the macro to continue. The warm up time for this macro is 2½ hours. When the macro has completed the warm-up period the message 'Operation Complete' is displayed on the screen. If the macro was called from another macro, such as the MERCURY macro, then control is given back to the calling macro and the calling macro will resume at the step after the call to the macro.

10.13 Replace the activated charcoal in the gas exhaust line annually. Note the change in the instrument maintenance logbook.

11.0 CHEMICALS AND REAGENTS

11.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Redistilled acids may be used if it has been demonstrated that the acid is free from contamination.

11.1.1 Concentrated hydrochloric acid, trace metal grade.

11.1.2 Concentrated nitric acid, trace metal grade

11.1.3 Concentrated sulfuric acid, trace metals grade.

11.2 **ASTM Type II water** (ASTM D1193). Deionized water is fed into an all glass distillation unit. The resulting distillate is immediately placed into a plastic container. Impurities are measured by the Inorganic group at TriMatrix. This is the only water acceptable for use in the Metals lab for dilutions or standard preparation.

11.3 **Standard stock solutions** are purchased primarily from Inorganic Ventures. All stock solutions are ICP grade single-element solutions at concentrations of 1000 or 10000 ppm.

11.4 Argon gas supply: Welding grade or better. Currently, this is plumbed from a liquid Ar tank located outside of the building. Ar is used as the carrier gas for analysis.

11.5 Potassium Persulfate, 5% solution (W/V). In a plastic 3L-glass container, place 150 g $K_2S_2O_8$ crystals. Add 3 L ASTM Type II water to the container. Place a stir bar in the solution and stir on a stir plate until all of the crystals have dissolved. This solution will take several hours to prepare. Keep the container closed when not in use to avoid contamination of the reagent. This reagent will be made fresh weekly, or sooner, if a precipitate has formed.

11.6 Potassium Permanganate, 5% solution (W/V). In a plastic 3-liter container, place 150 g $KMnO_4$ crystals. Add 3 L ASTM Type II water to the container. Place a stir bar in the solution and stir on a stir plate until all of the crystals have dissolved. Since this solution is nearly a saturated solution, this solution may take several hours to prepare. To check if the crystals have dissolved, a glass pipette may be used to probe the bottom of the container for excess crystals. If any of the solution is spilled, immediately clean up the spill with water. If a brownish stain remains, it may be removed from surfaces with hydroxylamine hydrochloride. If the solution touches exposed skin, the skin will turn brown. The brown discoloration is not harmful as long as the excess permanganate is washed off. The stain will wear off over time. Potassium permanganate will collect mercury if left exposed to the atmosphere. The container must be covered when not in use and should be stored in a dark cabinet to reduce the potential for auto-catalytic reduction.

11.7 Sodium Chloride Hydroxylamine Hydrochloride, 12% solution (W/V). In a plastic 3-liter container, place 360 g of sodium chloride and 360 g of hydroxylamine hydrochloride. Add 3 L of ASTM Type II water and a stir bar. Place the container on a stir plate and stir until all of the crystals have dissolved. This reagent must be prepared fresh daily.

11.8 Sulfuric Acid 0.5N. Rinse a clean 1 liter volumetric flask several times with ASTM Type II water. Place about 500 ml ASTM Type II water in the flask. Carefully add 14 ml concentrated sulfuric acid to the water. Carefully swirl the flask to mix the solution. Dilute to the mark with ASTM Type II water. Mix well.

11.9 Stannous Sulfate, 10% solution (W/V). Rinse a clean 500 ml volumetric flask several times with ASTM Type II water. Place about 250 ml 0.5 N H_2SO_4 in the flask. Add 50 g stannous sulfate and dilute the flask to volume with 0.5 N H_2SO_4. Mix well. When the crystals have gone into solution, filter through a 0.45 µm filter by using a vacuum apparatus and a side arm filtering flask. **NOTE:** This mixture is a suspension and must be stirred continuously during use, even after filtration.

12.0 STANDARDS PREPARATION

12.1 All standards are single-element standards. All standards are good for 1 day.

12.2 Preparation of the 10,000 ppb standard.

12.2.1 Rinse a clean 100 ml volumetric flask with ASTM Type II water several times.

12.2.2 Place about 20 ml of ASTM Type II water in the flask.

12.2.3 Add 0.5 ml concentrated trace metal grade HNO_3 to the flask and swirl.

12.2.4 Pipette 1 ml 1000 ppm stock standard solution into the volumetric flask.

12.2.5 Dilute the flask to the mark and mix well.

12.2.6 Update the stock standard logbook.

12.2.7 Transfer the standard number from the standard logbook to the volumetric flask.

12.3 Preparation of the 100 ppb standard.

12.3.1 Rinse a clean 100 ml volumetric flask with ASTM Type II water several times.

12.3.2 Place about 20 ml of ASTM Type II water in the flask.

12.3.3 Add 0.5 ml concentrated trace metal grade HNO_3 to the flask and swirl.

12.3.4 Pipette 1 ml 10,000 ppb stock standard solution prepared in Step 11.2 into the volumetric flask.

12.3.5 Dilute the flask to the mark and mix well.

12.3.6 Update the stock standard logbook.

12.3.7 Transfer the standard number from the standard logbook to the volumetric flask.

12.4 Preparation of working standards.

12.4.1 Six calibration standards are prepared for use in the initial calibration curve. The six standards include a blank, a low level standard at the reporting limit (nominally 0.2 µg/L), 3 mid level standards, and a high standard near the upper linear range point (typically 5 µg/L). The standards are prepared as follows. Rinse six clean 100 ml volumetric flasks several times with ASTM Type II water.

12.4.2 Label the flasks as follows:

5 µg/L Hg-100 ml volumetric flask
2 µg/L Hg-100 ml volumetric flask
1 µg/L Hg-100 ml volumetric flask
0.5 µg/L Hg-100 ml volumetric flask
0.2 µg/L Hg-100 ml volumetric flask
Hg blank-100 ml volumetric flask

12.4.3 Add approximately 20 ml ASTM Type II water to each flask.

12.4.4 Add 0.5 ml concentrated trace metal grade HNO_3 to each flask and swirl.

12.4.5 Pipet 5 ml of the 100 µg/L Hg standard and transfer it to the 100 ml flask labeled 5 µg/L Hg. Dilute to volume and mix.

12.4.6 Pipet 2 ml of the 100 µg/L Hg standard and transfer it to the 100 ml flask labeled 2 µg/L Hg. Dilute to volume and mix.

12.4.7 Pipet 1 ml of the 100 µg/L Hg standard and transfer it to the 100 ml flask labeled 1 µg/L Hg. Dilute to volume and mix.

12.4.8 Pipet 0.5 ml of the 100 µg/L Hg standard and transfer it to the 100 ml flask labeled 0.5 µg/L Hg. Dilute to volume and mix.

12.4.9 Pipet 0.2 ml of the 5 µg/L Hg standard and transfer it to the 100 ml flask labeled 0.2 µg/L Hg. Dilute to volume and mix.

12.4.10 Dilute the flask labeled Hg blank to volume and mix well.

12.4.11 All working standards must be digested within 8 hours of preparation.

12.4.12 Complete the standards log book (see Appendix J).

12.4.13 Transfer the information from the standard logbook to the standard flasks and the ID/Wt sheet used for the analysis.

13.0 SAMPLE PREPARATION

13.1 All samples, standards, and quality control check samples must be digested before analysis.

13.2 Fill out the ID/WT sheet for the analysis. Each line on the ID/WT sheet represents a discreet autosampler position. If a sample needs a SPK and an MSD, then the sample will require three autosampler positions. If a dilution is to be performed on the sample, place the dilution factor in the column provided. NOTE: Continuing calibration verifications and blanks do not need to be placed in between samples, the PS200 will automatically go back to a special vial for these samples.

13.3 Load the autosampler tray with the samples to be prepared.

13.3.1 The first rack, the standards rack, contains 14 autosampler positions. Place seven 30 ml vials in autosampler positions S1 through S7. Autosampler positions S1 through S6 are reserved for standard solutions. S7 will always contain an empty vial for the unit to rinse into. Place 24 ml

of the standard solutions into the appropriate autosampler vials. Please refer to Table 1 for autosampler positions for the standards.

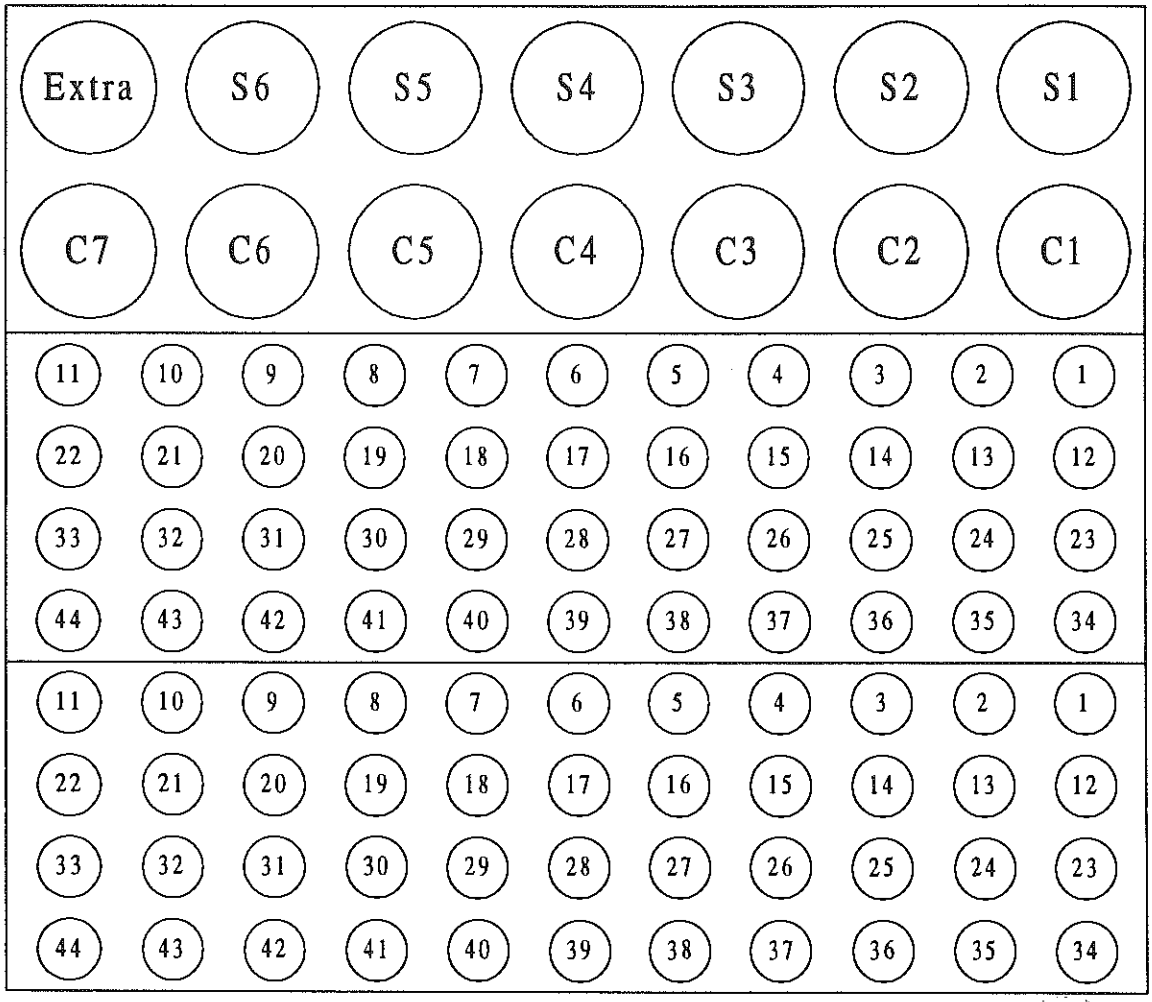
13.3.2 Place three 30 ml vials in autosampler positions C1 through C3. Place 24 ml of the quality control solutions into the appropriate autosampler vials. Please refer to Table 1 for autosampler positions for the quality control samples.

Table 1. Autosampler Positions for Standards and QCs

Autosampler Position	Standard Concentration (ppb)/Name
Rack 0, Position 1 (S1)	0 (Blank)
Rack 0, Position 2 (S2)	0.2
Rack 0, Position 3 (S3)	0.5
Rack 0, Position 4 (S4)	1.0
Rack 0, Position 5 (S5)	2.0
Rack 0, Position 6 (S6)	5.0
Rack 0, Position 8 (C1)	0 (Blank)
Rack 0, Position 9 (C2)	2.0 (ICV/CCV)
Rack 0, Position 10 (C3)	LCS
Rack 0, Position 11 (C4)	LCS

13.3.3 Load the samples into the autosampler trays. Place a vial containing 8 ml of the appropriate sample into its assigned position. While loading the tray, frequently refer to the ID/WT sheet to ensure that the sample is going into the correct autosampler position. Please refer to Figure 1 to determine how the autosampler rack is numbered.

Figure 1. Autosampler Rack Setup for the AP200 and PS200



13.4 Add concentrated H_2SO_4 to all standards and samples.

13.4.1 To all standards add 1.25 ml

13.4.2 To all samples add 0.4 ml

13.5 Add concentrated HNO_3 to all standards and samples.

13.5.1 To all standards add 0.625 ml

13.5.2 To all samples add 0.2 ml

13.6 Add $KMnO_4$ to all standards and samples and wait at least 15 minutes before proceeding to 13.7.

13.6.1 To all standards add 7.5 ml

13.6.2 To all samples add 2.5 ml

13.7 Add concentrated K_2SO_4 to all standards and samples.

13.7.1 To all standards add 2 ml

13.7.2 To all samples add 0.66 ml

13.8 Heat water in a roasting pan to 95°C.

13.9 Insert the standard vials and sample vials into the water bath and place tin foil around the sample racks to keep the heat in.

13.10 Once the water bath reaches 95°C again, set and start a 2 hour timer. After 2 hours, remove the samples from the water bath and allow to cool.

13.11 Once the standards and samples have cooled, add $NH_4OH{\bullet}HCl$.

13.11.1 To all standards add 3.0 ml

13.11.2 To all samples add 1.0 ml

13.12 Print and fill out a LIMS pretreatment benchsheet. See Appendix F.

13.13 Pretreat the samples on LIMS. See Appendix C.

13.14 Fill out the mercury digestion logbook. See Appendix D.

14.0 CALIBRATION PROCEDURES

14.1 Calibration of the instrument must be performed every 24 hours or for every batch of samples that were prepared in the same manner, whichever is more frequent. For example, if a soil calibration was performed at 8 AM and a water run is to be performed at 5 PM of the same day, a new calibration curve must be performed with standards prepared with the samples to be analyzed. A blank and five standards are run to comprise the initial calibration curve, as described in section 11.4. A minimum of a blank and three standards are required to be included in the initial calibration curve.

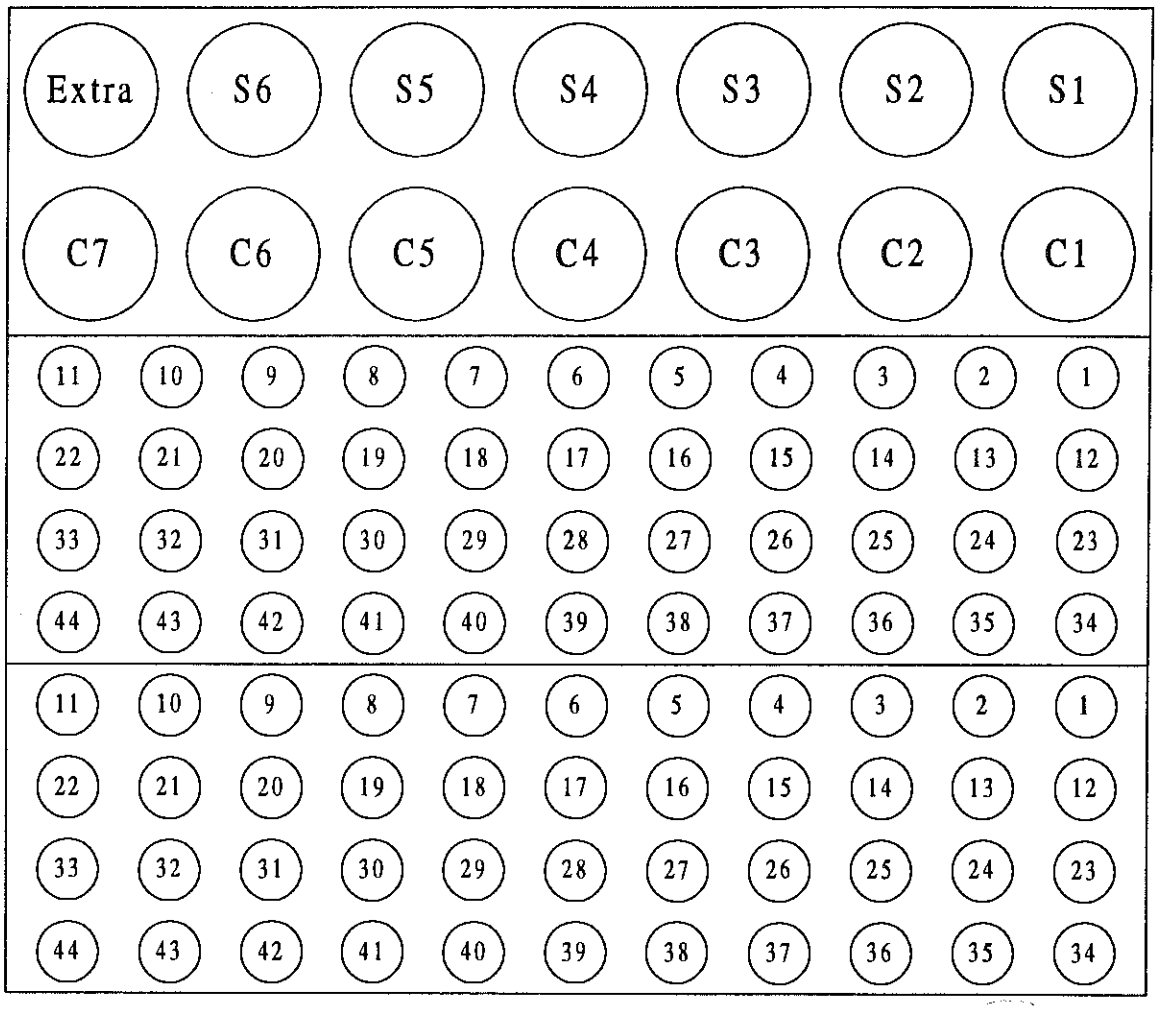
14.2 Start the instrument software as described in Section 14. Perform a COLDSTRT or a WARMSTRT, whichever is needed.

14.3 Load the autosampler tray with the appropriate standards. See Table 2 for autosampler positions. Rack 0 is the rack that is furthest away from the front of the instrument. See Figure 2 for autosampler position designation.

Table 2. Autosampler Positions for Standards

Autosampler Position	Standard Concentration (ppb)
Rack 0, Position 1 (S1)	0 (Blank)
Rack 0, Position 2 (S2)	0.2
Rack 0, Position 3 (S3)	0.5
Rack 0, Position 4 (S4)	1.0
Rack 0, Position 5 (S5)	2.0
Rack 0, Position 6 (S6)	5.0

Figure 2. Autosampler Position Designation



14.4 There are currently three ways to calibrate the instrument. Although the three methods are different in the keystrokes used, they are essentially performing the same task.

14.4.1 Method 1: Allow the MERCURY macro to run the standards unattended. This method will automatically initialize all parameters, run the standards, check the QC, run samples, and run periodic QC.

14.4.1.1 Start the MERCURY macro. When the PS200 software is booted up, the MERCURY macro is automatically invoked. If, for some reason the macro is stopped, the macro can be restarted by pressing <F2> then typing in MERCURY and pressing <Enter>.

14.4.1.2 Follow the direction outlined in Section 14 until the software asks if standards should be ran. Answer 'Y' to this question.

14.4.1.3 The instrument will automatically run the standards and plot the calibration curve when finished. Skip to Step 13.5.

14.4.2 Method 2: Use the RUNSTDS macro to run the standards unattended. This method will run the standards unattended and then stop. The user will have to either invoke the MERCURY macro again to restart the analysis in unattended mode or else the run will have to be performed manually.

14.4.2.1 Set up the instrument as described in Section 14. Perform a WARMSTRT or a COLDSTRT, if needed.

14.4.2.2 Start the macro by pressing <F2>, then type in RUNSTDS and press <Enter>.

14.4.2.3 The instrument will automatically run the standards and plot the calibration curve when finished. Skip to Step 13.5.

14.4.3 Method 3: Run each standard individually. This method needs constant operator attendance and should not be used if the entire curve is to be ran. The operator is responsible for checking all values before running the analysis if this method is used.

14.4.3.1 Press <F6> (Standard).

14.4.3.2 The software will ask for the standard number to run. Enter the standard number that should be analyzed. Do not enter the standard concentration, only the standard position. Refer to Figure 2 for the standard autosampler position.

14.4.3.3 Repeat steps 13.4.3.1 and 13.4.3.2 for the remaining standards that need to be ran.

14.4.3.4 When finished running the standards, go to the calibration page by pressing <F1> (Main Menu) then pressing <C> (Calibration) <L> (Line calibration). At this point a plot of the calibration should be displayed.

14.4.3.5 Press <A> to accept the calibration curve.

14.5 The correlation coefficient 'r' must be equal to or greater than 0.995. If the correlation coefficient is not equal to or greater than 0.995, up to 2 of the standard results may be deleted from the curve, excluding the blank and the low level standard run at the reporting limit. If the high level standard is one of the results deleted, the linear range of the curve has been decreased, and required sample dilutions will be adjusted accordingly. If the deletion of standards results does not solve the problem, corrective actions will be taken, including re-analysis of individual points, or the entire initial calibration curve.

14.5.1 Rerunning a point in the calibration curve.

14.5.1.1 Press <F6> (Standard).

14.5.1.2 The software will ask for the standard number to run. Enter the standard number that should be analyzed. Do not enter the standard concentration, only the standard position. Refer to Figure 2 for the standard autosampler position.

14.5.1.3 Repeat steps 13.5.1.1 and 13.5.1.2 for the remaining standards that need to be ran. **NOTE:** The software will not automatically re-calculate the correlation coefficient. The user must press <A> to re-calculate the coefficient.

14.5.2 Deleting a point in the curve that is not correct.

14.5.2.1 Since it is possible that there was a determinate error in the preparation of the standards, standard points may be dropped if they appear to significantly deviate from the curve. At least 3 standards and the blank must remain in the curve for the calibration curve to be valid.

14.5.2.2 Use the arrow keys to highlight the point that is to be deleted from the curve.

14.5.2.3 Press <Enter> to delete the point from the calibration curve.

14.5.2.4 Press <A> to re-calculate the calibration curve and correlation coefficient.

14.5.3 Add a previously deleted point back to the curve.

14.5.3.1 If a calibration point has been deleted by accident, or if it was deleted to check its affect on the remaining curve, the point may be added back without re-running the point. At least 3 standards and the blank must remain in the curve for the calibration curve to be valid.

14.5.3.2 Use the arrow keys to highlight the point that is to be added back to the curve.

14.5.3.3 Press <Enter> to add the point to the calibration curve.

14.5.3.4 Press <A> to re-calculate the calibration curve and correlation coefficient.

14.6 If the MERCURY macro was used to produce the analytical curve, press <F2> when the curve is acceptable. The software will double check that the correlation coefficient is correct, then print the analytical curve. The macro will then automatically start analyzing the quality control samples and samples. See Section 14 for a more in depth discussion on performing the analysis.

14.7 If the RUNSTDS macro was used to produce the analytical curve, press <F2> when the curve is acceptable. The software will double check that the correlation coefficient is correct, then print the analytical curve. The macro will then end. At this point, the quality control samples must be analyzed. If an unattended mode of operation is preferred, start the MERCURY macro by pressing <F2> and then

typing in MERCURY<Enter>. Performing the analysis manually is beyond the scope of this procedure. See Section 14 for a more in depth discussion on performing the analysis.

14.8 If the curve was constructed by manually running the standards, double check that the curve is accepted by pressing <A>. Check to ensure that the correlation coefficient is still 0.995 or greater. If the correlation is not at least 0.995, go back to step 13.5 and edit the calibration. If the correlation is okay, print the curve by pressing <F4> (Print Screen). At this point, the quality control samples must be analyzed. If an unattended mode of operation is preferred, start the MERCURY macro by pressing <F2> and then typing in MERCURY<Enter>. Performing the analysis manually is beyond the scope of this procedure. See Section 14 for a more in-depth discussion on performing the analysis.

15.0 ANALYTICAL PROCEDURE

15.1 This procedure assumes that the user has been introduced to the software either by reading the software manual or by experienced metals personnel. Advanced topics, such as how to replace the mercury source lamp are beyond the scope of this method. In this case, the user should reference the instrument manual.

15.2 Make sure that the argon supply is on. There is a valve behind the instrument that supplies the PS200 instrument. Make sure that the valve is open.

15.3 Turn on the instrument on if it is not already on. The power button for the instrument is the blue button on the front of the instrument. If the instrument fails to turn on, contact the metals lab supervisor.

15.4 Turn the computer and printer on if they are not turned on. If the computer fails to boot, contact the metals lab supervisor.

15.5 Turn the lamp on. The lamp power button is the green button on the front of the instrument. Allow the lamp to warm up for at least ½ hour before testing the aperture. If the lamp does not seem to be working, contact the metals lab supervisor.

15.6 The computer will automatically start the MERCURY macro. Stop the macro by pressing <F10> (Stop).

15.7 Place the stannous sulfate line (the line connected to the red/red tubing) and the sample line (the line connected to the black Viton tubing) in the wash vessel. Fill the wash vessel with 10% HCl solution.

15.8 Check the peristaltic tubing. If the tubing is blocked or badly worn, replace it with new tubing.

15.9 Clamp the tubing in place. Make sure that the peristaltic tubing is in a straight line over the pump rollers. Lift the red lever on the pump manifold to press the tubing against the rollers.

15.10 Start the pump. Go to the **Instrument** screen by pressing **I**. Press **O** to go to the **Operation** screen. Press **R O** to start the pump.

15.11 Turn on the Argon carrier gas. While in the **Instrument Operation** screen, press **G O** to turn on the carrier gas.

15.12 Check the peristaltic tubing to ensure that the pump is drawing liquid. Lift the sample line out of the rinse solution to see if the pump will pull air. Check the stannous sulfate line the same way. Watch the drain line right after the liquid/gas separator to see if bubbles are being drawn through the tubing. If none of the tubing is drawing, make sure that the pump is turning. If a single piece of tubing is not drawing, try to increase the tension to make the tubing draw by lifting the red lever on the pump manifold higher. If liquid is still not being drawn, try changing the tubing (See Section ####). If the pump still does not draw, a clog should be suspected. Please see the metals lab supervisor for help in finding and correcting the cause of the clog.

15.13 Fill the drying tube with drying agent. Currently, the metals lab is using Magnesium Perchlorate (Anhydrone) as the drying agent for mercury determinations.

15.13.1 Place a small amount of glass wool in one end of the drying tube. There should be just enough glass wool to keep the drying agent from falling out of the tube. Do not put too much glass wool in the end of the tube as this may restrict gas flow through the drying tube.

15.13.2 While wearing gloves, carefully fill the drying tube with fresh magnesium perchlorate. Fill the tube up to the neck of the tube. Gently tap the bottom of the tube on the counter to help the crystals settle into place. Do not over pack the tube as this will restrict the gas flow through the tube. Fill the tube up again within ¾ inch of the end of the tube.

15.13.3 Place a small amount of glass wool in the end of the drying tube. There should be just enough glass wool to keep the drying agent from falling out of the tube. Do not put too much glass wool in the end of the tube as this may restrict gas flow through the drying tube.

15.13.4 Check the O-rings on the drying tube endcaps for wear. Replace these O-rings if there is obvious wear.

15.13.5 Place the drying tube end caps on the end of the drying tube. Push the ends on until they stop. Tighten the nut on the endcaps until snug. Do not over tighten the endcaps.

15.13.6 Place the drying tube in its holder on the instrument.

15.14 If the lamp has been on for at least ½ hour, test the aperture.

15.14.1 Start the APERTEST macro.

15.14.1.1 Press <F2> (Macro).

15.14.1.2 Type in APERTEST, then press <Enter>.

15.14.2 The macro will now start to display some numbers on the screen. These numbers are the readings for the aperture and they represent the difference in intensity between the sample beam of the instrument and the reference beam.

15.14.3 The aperture reading must be 0±100, preferably 0±20. If the reading is not within specifications, adjust the aperture until the value is within range. Adjustment should be done as quickly as possible so that the temperature of the flow cell does not change significantly.

15.14.3.1 Remove the front cover from the instrument to reveal the flow cell. Push the cover up and then pull forward to remove.

15.14.3.2 Remove the Allen wrench from the front panel. The wrench is used to turn the aperture screws.

15.14.3.3 There are two screws on the flow cell at the right-hand end of the flow cell. Always adjust the screw that has been turned into the flow cell the furthest.

15.14.3.4 If the reading is negative, turn the screw clockwise until the reading is zero.
NOTE: In order to obtain an accurate reading, let go of the Allen wrench while taking the reading. Any pressure applied to the flow cell during the reading will change the reading.

15.14.3.5 If the reading is positive, turn the screw counter-clockwise until the reading is zero.
NOTE: In order to obtain an accurate reading, let go of the Allen wrench while taking the reading. Any pressure applied to the flow cell during the reading will change the reading.

15.14.3.6 Repeat steps 14.14.3.4 and 14.14.3.5 until the aperture reading is within the range 0±20.

15.14.3.7 Replace the Allen wrench in the front cover of the instrument.

15.14.3.8 Replace the front cover on the instrument. Make sure that the cover is seated firmly on the instrument and that the cover is flush with the instrument.

15.14.4 End the APERTEST macro by pressing <F8>. The macro will take one last reading of the aperture and print that value out on the printer.

15.15 Enter the sample identifications into the computer.

15.15.1 Go to the main menu by pressing <F1>.

15.15.2 Select the **Autosampler** screen by press **A**.

15.15.3 Enter the **Rack entry** screen by pressing **R**.

15.15.4 At the bottom of the screen, there will be a prompt for the rack name. The rack name is a combination of the month, day, analysis number of the day, and rack number of the analysis in a specific order. The format is:

MDDRA-N

Where:

M is the coded month

DD is the two digit date of the month

R is the letter R

A is the numeric representation of the number of separate analyses that have been performed that day. An analysis is defined as a set of samples that are digested together. For example, if a water digestion is analyzed first thing in the day, then **A** would be 1. If a soil digestion is then analyzed during that day, **A** would be 2.

N is the numeric representation of the number of separate racks that have been performed for a given analysis for that day. For example, if a soil digestion has 5 racks, the first rack would have an **N** value of 1, the second a value of 2, the third a value of 3, and so on.

For example, for the first rack of the first run analyzed on October 6, the rack name would be C06R1-1.

Type in the rack name in the space provided and press <Enter>. If the rack name does not exist, the computer will ask if it should create a new rack name. Answer 'Y' and press <Enter>. Place the rack name on the autosampler ID/WT sheet in the space provided.

15.15.5 Press the <Insert> key once to begin editing the contents of the rack.

15.15.6 The first column, labeled 'cup', contains the autosampler position number that corresponds to the ID/WT sheet used for setting up the autosampler tray. This field may not be edited.

15.15.7 The second column, labeled 'Id', will contain the sample identification that is located on the ID/WT sheet. The number or identification put in this column will be the LIMS sample number for the sample.

15.15.8 The third column, called 'Extended Id', while not commonly used, may be used to further identify the sample.

15.15.9 The third and fourth columns on the computer screen will contain the sample digestion weight and volume for the sample. For example, if 0.1 g of sample was digested, then the dilution factor would be 0.1 in the weight column and 100 in the volume column (0.1g was digested into 100 ml final solution). If a subsequent dilution is performed on the sample, then the final volume is multiplied by that dilution factor. For example, if in the above example, the final solution is then diluted 10X, then the final volume would be 1000. Please see the metals lab supervisor for further instruction on this topic.

15.15.10 There are a total of 44 positions for each tray. To go down to the next page of autosampler positions, press <Page Down>. To go up to the previous page, press <Page Up>.

15.15.11 When the ID/WT sheet is completely entered into the computer for a rack, press 'E' to exit.

15.15.12 Repeat steps 14.15.4 through 14.15.11 for the remaining racks.

15.16 Start the MERCURY macro.

15.16.1 Press <F2> (Macro).

15.16.2 Type in MERCURY in the space provided, then press <Enter>.

15.17 At this point the MERCURY macro should start initializing the system. The macro will ask the user a series of questions to determine the state of the instrument. If the macro fails to start or if there are any problems from this point on, contact the metals lab supervisor.

15.18 The computer will ask 'Would you like to do a warm start? <Y/N>'. The warm start macro is used to prepare the PS200 200 for operation from the short-term shut down. If the lamp has been shut off for more than 1 hour, and the instrument has been left on, enter "Y". See Section 9.9 for a description of the WARMSTRT macro.

15.19 The macro will then ask the user 'Would you like to test the aperture? <Y/N>'. If the aperture has already been tested, answer 'N', otherwise answer 'Y'. For a discussion on the APERTEST macro, see Section 14.4.

15.20 A data file name must now be entered. The data file name must be unique, otherwise, the data will be appended to another data file. The data file name is a combination of the month, day of the month, and analysis number of the day. The format is:

MDDRA

Where:

M is the coded month

DD is the two digit date of the month

R is the letter R

A is the numeric representation of the number of separate analyses that have been performed that day. An analyses is defined as a set of samples that are digested together. For example, if a water digestion is analyzed first thing in the day, then A would be 1. If a soil digestion is then analyzed during that day, A would be 2.

For example, for the first run analyzed on October 6, the data file name would be C06R1.

Type in the data name in the space provided and press <Enter>. If the data name does not exist, the computer will ask if it should create a new one. Answer 'Y' and press <Enter>. Place the data file name on the autosampler ID/WT sheet in the space provided.

15.21 The instrument will now prompt for the rack name and the autosampler positions that should be analyzed.

15.21.1 At the prompt 'Enter rack name (ENTER for none)', place the name of the first rack to be analyzed. If there is no rack, press the <Enter> key to skip this entry.

15.21.2 Type in the first autosampler position that is to be analyzed. Again, press <Enter> if there are no samples in the first physical rack to analyze.

15.21.3 Type in the last autosampler position to be analyzed on the first rack. Press <Enter> if there are no samples to analyze on the rack.

15.21.4 At the prompt 'Enter rack name (ENTER for none)', place the name of the second rack to be analyzed. If there is no rack, press the <Enter> key to skip this entry.

15.21.5 Type in the first autosampler position that is to be analyzed. Again, press <Enter> if there are no samples in the second physical rack to analyze.

15.21.6 Type in the last autosampler position to be analyzed on the second rack. Press <Enter> if there are no samples to analyze on the rack.

15.22 When the printer is done printing, the macro will take the user to the check sample screen. The user must verify that the values that the macro is putting in are okay. If the values entered for the BLK, the ICV/CCV, or the LCS are not correct, change them when prompted. If the values need to be updated in the macro, contact the metals lab supervisor.

15.23 The macro will now pause so that the user may check the values that have been entered automatically by the macro. This pause also allows the user to correct any mistakes that were made when entering data at the macro prompts. This SOP will not attempt to describe all of the information that may be edited. The user may refer to the instrument manual or may contact the metals lab supervisor if there is something that must be changed before beginning the analysis. When all of the values are okay, press <F2> to resume the macro.

15.24 As an added protection, the macro will ask 'Are you sure you want to start? <Y/N>'. Answer with the appropriate response. The macro will not continue until 'Y' is entered.

15.25 The computer will ask 'Do standards need running? <Y/N>'. The instrument must be calibrated every 24 hours or every time that a new digestion batch is started. Answer the question appropriately. If the standards do need to be ran, see Section 13 for a detailed explanation of the calibration sequence.

15.26 When the standards are complete, the instrument will automatically analyze the ICB. The amount found in the ICB must not be greater than the absolute value of the reporting limit. If at any point in the decision tree below the ICB is within the limits, the macro will jump to step 14.27.

15.26.1 If the ICB does not meet the criteria, the macro will ask the user to place a new vial of the blank in autosampler position C1. Press and key to continue.

15.26.2 The instrument will then analyze the new ICB. If the ICB still does not meet the criteria, then the macro will autozero the instrument and rerun the ICB.

15.26.3 If the ICB does not read back within limits, the macro will essentially jump back to step 14.26.1. Please note that there is a possibility of an infinite loop occurring at this step. If the analysis of the ICB still does not pass the criteria after the instrument has been autozeroed, stop the macro and contact the metals lab supervisor for assistance. Analysis cannot continue until an acceptable ICB has been analyzed.

15.27 When the ICB reads back within limits, the ICV will automatically be analyzed. The ICV is the midpoint calibration standard analyzed as a sample with the concentration being read from the analytical curve. The percent recovery for the ICV must be within the control limits of 80%-120% of the true value. If the ICV recovers within the control windows, the macro will jump to Step 14.28.

15.27.1 If the ICV fails to recover within the control limits, the macro will ask the analyst to place a new vial of the ICV in autosampler position C2. When this is complete, press any key to continue the analysis.

15.27.2 If the ICV fails again, corrective action measures must be implemented. If a mechanical failure can be found which has caused the out of control ICV, correct the problem and return to section 14.26, ICB analysis. If other corrective action procedures are required, such as gas flow adjustments or tubing replacement, the initial calibration sequence must be initiated again. Analysis may not begin until an acceptable ICV has been analyzed.

15.28 The macro will now analyze an independent standard called the Laboratory Control Sample (LCS). The LCS is a second source purchased standard, at a nominal concentration of 3.0 µg/L. The percent recovery must fall within the LIMS (Laboratory Information Management System) control limit for this type of QC. Please refer to the current LIMS control limits for the windows.

15.28.1 If the LCS does not fall within established control limits, the macro will ask the user to place another vial of the LCS in autosampler position C3. Press <Enter> to continue.

15.28.2 If the LCS still does not meet the criteria, then the macro will ask the user to prepare a new LCS and to place the vial for the new LCS in autosampler position C3. Press any key to continue.

15.28.3 If the LCS still does not work, stop the macro and contact the metals lab supervisor for assistance. Analysis may not begin until an acceptable LCS has been analyzed.

15.29 The autosampler will now analyze 10 sample vials. If there are less than 10 vials left on the tray, then the autosampler will only analyze those samples. If the nser needs to pause at any time during the analysis, press <F8>. The autosampler will stop after the current sample and wait until the <F8> key is pressed

again. If the user presses the <F10> key, then the macro will stop immediately. The only way to resume a stopped analysis is to go to step 14.16 and restart the MERCURY macro.

15.30 When the autosampler has completed the analysis of ≤10 samples, the instrument will automatically analyze the CCB. The amount found in the CCB must not be greater than the absolute value of the reporting limit. If at any point in the decision tree below the CCB is within the limits, the macro will jump to step 14.31.

15.30.1 If the CCB does not meet the criteria, the macro will ask the user to place a new vial of the blank in autosampler position C1. Press and key to continue.

15.30.2 The instrument will then analyze the CCB again. If the CCB still does not meet the criteria, corrective actions will be taken. If a high level sample is carrying over, blanks will be analyzed until the system is clean. If there is no apparent cause for the out of control CCB, the analyst will allow the macro to autozero the instrument, and the CCB will be re-analyzed. If an autozero is required, all samples analyzed since the last acceptable CCB will be re-analyzed.

15.30.3 Please note that there is a possibility of an infinite loop occurring at this step. If the CCB still does not work after the instrument has been autozeroed, stop the macro and contact the metals lab supervisor for assistance. An acceptable CCB is required for sample data to be acceptable.

15.31 When the CCB reads back within limits, the CCV will automatically be analyzed. The CCV is the midpoint calibration standard analyzed as a sample with the concentration being read from the analytical curve. The percent recovery for the CCV must be within the control limits of 80%-120% of the true value. If the CCV recovers within the control windows, then the macro will jump to Step 14.32.

15.31.1 If the CCV does not fall within established control limits, the macro will ask the user to place another vial of the CCV in autosampler position C2. Press <Enter> to continue.

15.31.2 If the CCV still does not meet the criteria, then the macro will ask the user to prepare a new CCV and to place the vial for the new CCV in autosampler position C3. Press any key to continue.

15.31.3 If the CCV still does not work, stop the macro and contact the metals lab supervisor for assistance. An acceptable CCV is required for sample data to be acceptable.

15.32 If the CCV recovers within control limits, then start again at Step 14.29 with the next set of samples to be analyzed. If there are no more samples to analyze, then go to Step 14.33.

15.33 Check over the raw data to make sure that all of the samples are within the calibration range of the instrument. If any samples are above the calibration range of the curve, mark the sample number and appropriate dilution factor. Dilutions will need to be ran with the next batch.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The concentration of each sample is read directly from the computer printout. Dilution factors should be taken into account in the ID/WT file.

16.1.1 Assuming that the instrument did not correct a concentration due to analyst error, the following calculation would be used:

$$C_{Final} = C_{Instr} * DF_{Digest} * DF_{Subseq}$$

where

C_{Final} is the final reported concentration of the analyte
C_{Instr} is the concentration as read from the instrument data printout
DF_{Digest} is the digestion dilution factor
DF_{Subseq} is any dilution done subsequent to the digestion dilution

16.2 All samples should be reported to the correct number of significant figures. The significant figure truncation should not be performed until all data calculation have taken place.

16.2.1 Solid samples must be reported in mg/kg.

16.2.1.1 For sample concentrations <100 mg/kg, report 2 significant figures.

16.2.1.2 For sample concentrations ≥100 mg/kg, report 3 significant figures.

16.2.1.3 For QC, always report one additional significant figure.

16.2.2 Aqueous samples must be reported in ug/L.

16.2.2.1 For sample concentrations <1 ppb, report 1 significant figure.

16.2.2.2 For sample concentrations ≥1 ppb and <100 ppb, report 2 significant figures.

16.2.2.3 For sample concentrations ≥100 ppb, report 3 significant figures.

16.2.2.4 For QC, always report one additional significant figure.

16.2.3 Extracted samples for all metals must be reported in mg/L.

16.2.3.1 For sample concentrations <0.001 mg/L, report 1 significant figure.

16.2.3.2 For sample concentrations ≥0.001 mg/L and <0.100 mg/L, report 2 significant figures.

16.2.3.3 For sample concentrations ≥0.100 mg/L, report 3 significant figures.

16.2.3.4 For QC, always report one additional significant figure.

17.0 DATA REPORTING AND DELIVERABLES

17.1 See appendices F, H, I, and J for data reporting.

18.0 QUALITY ASSURANCE

18.1 All quality control data should be maintained and available for easy reference or inspection.

18.2 A calibration curve must be prepared each day with a minimum of a reagent blank and three standards. The correlation coefficient must be ≥ 0.995. If this fails the problem must be corrected.

18.3 IDL and MDL studies must be performed on an annual basis.

18.3.1 To calculate an IDL, analyze ten cups of Blank solution in series. Calculate the standard deviation of a small population, and multiply this result by three. There is also a spreadsheet located on the computer network that will perform this calculation for you. Please see the metals lab supervisor if you need assistance in using this program.

18.3.2 To calculate an MDL, analyze ten cups of a low concentration standard, typically at a concentration at or near the detection limit. Calculate the standard deviation of a small population and multiply the result by the Student's T value for (n-1) degrees of freedom. If the concentration of the standard ran is greater than ten times the calculated MDL, and the concentration of the standard ran is above the detection limit reported to clients, the MDL must be performed at lower concentration. If the standard concentration is less than ten times the calculated MDL or if the standard used for the analysis was at or below the lowest reporting limit on LIMS, the MDL is acceptable. There is also a spreadsheet located on the computer network that will perform this calculation for you. Please see the metals lab supervisor if you need assistance in using this program.

18.4 Dilute, reprep, and reanalyze all samples that have concentrations greater than the highest standard of the analytical curve.

18.5 Include a minimum of one laboratory blank per sample digestion batch to determine if contamination or any memory effects are occurring. This laboratory blank must be carried through the sample preparation procedure.

18.6 Analyze one spike and one matrix spike duplicate (MSD) at a frequency of at least 1 in 20. A spike and matrix spike duplicate are samples into which a calculated extra amount of metal is pipetted in. Currently, the spike concentration is at 2.5 µg/L. The spike measures the accuracy of the sample preparation method and the MSD checks the precision of the method.

18.7 **Standard addition**: The Method of Standard Additions (MSA) shall be used for all EP extracts. MSA must also be performed on all TCLP extracts that have spike recoveries less than 50%. The standard-addition technique involves adding known amounts of standard to one or more aliquots of the process sample solution. This technique compensates for a sample constitute that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct additive interferences that cause a baseline shift. The simple version of this technique is the single addition method, in which identical aliquots of the sample solution, each of volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_X is calculated:

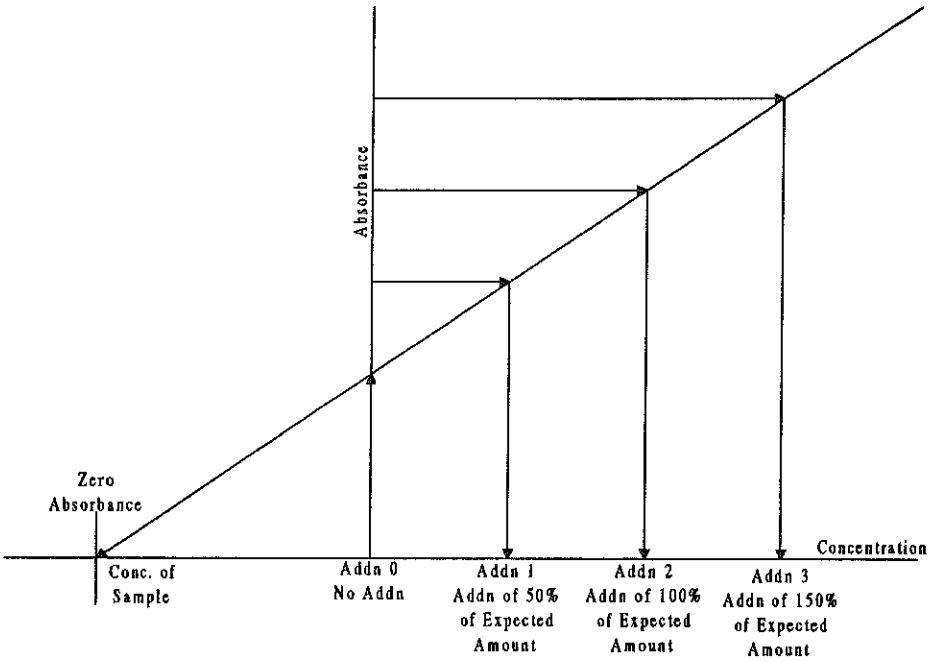
$$C_X = \frac{S_B * V_S * C_S}{(S_A - S_B) * V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear and the correlation coefficient must be ≥ 0.995.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 2.

Figure 2 An Example of an MSA curve



NOTE: A method of standard addition must be performed on any TCLP sample whose spike recovery is not greater than 50%.

18.8 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

NOTE: Steps 18.8.2 through 18.8.6 must be performed every time the instrument is calibrated.

18.8.1 Calibrate the instrument using at least three standards and a blank.

18.8.2 An ICB (Initial Calibration Blank) is analyzed after the calibration. The results of this blank are to be within ± 0.2 µg/L. If the blank is not within ± 0.2 µg/L, correct the problem, and restart the analysis from the beginning.

18.8.3 An ICV (Initial Calibration Verification) is placed after the ICB. Percent recovery limits are 80% to 120% of the concentration. If the percent recovery for this standard is not within the acceptance limits, correct the problem, re-calibrate if necessary, and restart the analysis.

18.8.4 An LCS (Laboratory Check Standard), which must come from a different primary source than the calibration standards, is placed after the ICV in each run. At the time of this revision, the diluted LCS was at a concentration of 3.0 µg/L. Percent recovery limits are 80% to 120% of the concentration unless control limits have been established. If the percent recovery for this standard is not within the acceptance limits, correct the problem. If the instrument had to be re-calibrated, restart the analysis from the beginning.

18.8.5 Verify the calibration after every 10 samples.

18.8.5.1 A CCV (Continuing Calibration Verification) is analyzed after every 10 samples, or sooner. Percent recovery limits are 80% to 120% of the concentration. If the percent recovery for this standard is not within the acceptance limits, correct the problem. When the problem has been corrected, analyze a CCV. If the CCV is within control limits, restart the analysis from the last good ICV or CCV. If the CCV is not within the control limits, repeat steps 18.8.1 through 18.8.4, and then reanalyze all samples since the last good ICV or CCV.

18.8.5.2 A CCB (Continuing Calibration Blank) is analyzed after the CCV. The results of this blank are to be within ± 0.2 µg/L. If the blank is not within ± 0.2 µg/L, correct the problem, and restart the analysis from the last good CCB or ICB.

18.8.6 At the end of each run, verify the calibration.

18.8.6.1 A CCV (Continuing Calibration Verification) is analyzed after every 10 samples, or sooner. Percent recovery limits are 80% to 120% of the concentration. If the percent recovery for this standard is not within the acceptance limits, correct the problem. When the problem has been corrected, analyze a CCV. If the CCV is within control limits, restart the analysis from the last good ICV or CCV. If the CCV is not within the control limits, repeat steps 18.8.1 through 18.8.4, and then reanalyze all samples since the last good ICV or CCV.

18.8.6.2 A CCB (Continuing Calibration Blank) is analyzed after the CCV. The results of this blank are to be within ± 0.2 µg/L. If the blank is not within ± 0.2 µg/L, correct the problem, and restart the analysis from the last good CCB or ICB.

18.9 A new analytical curve must be ran every 24 hours.

18.10 If the % RSD of the replicates for a sample is greater than 20% and the concentration of the sample is greater than the reporting limit, reanalyze the sample once. If the % RSD is again greater than 20% on a sample, qualify the data with data Qnalifier number 10 "Duplicate injection precision not met for this analysis. The corresponding sample result must be considered estimated".

19.0 ANALYST CERTIFICATION/METHOD VALIDATION

19.1 Before the analysis of any actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running a one time analyst certification. While the analyst certification is not instrument dependent, this certification is required on every instrument that will be running samples to demonstrate instrument ability to generate acceptable accuracy and precision.

19.2 Prepare a quality control check sample spiking standard at a level that will give concentrations 1 mg/L.

19.3 Analyze the four distilled check samples following the SOP.

19.4 Calculate the average recovery (x) in mg/L, and the standard deviation of the recovery (s) in mg/L, for each analyte using the four results.

19.4.1 For each analyte x must be in the range 70-130% and s must be less than or equal to 20. If s and x for all analytes meet the acceptance criteria, the analyst certification is good. The analyst and the system are now authorized to run samples by this method. If any individual s exceeds the precision limit or any individual falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

19.4.2 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to 19.5.

19.5 Locate and correct the source of the problem and repeat the test for all analytes that failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds beginning with Section 19.1. Samples may not be analyzed by any analyst or on any instrument until the analyst certification has been successfully completed. Copies of the successful analyst certifications/method validations spreadsheet and raw data should be given to the Quality Assurance Manager.

20.0 REFERENCES

20.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, September, 1994, Method 7470A, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)".

20.2 *Methods for the Determination of Metals in Environmental Samples,* Supplement I, May 1994, Revision 5.4, EMMC Version, "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry", Method 245.1, Revision 3.0, May, 1994.

20.3 Gaskill, A, Compilation and Evaluation of RCRA Method Performance Data Work Assignment #2, EPA Contract No. 68-01-7075, September 1986.

20.4 Leeman Labs PS Series ICP/Eschelle Spectrometers Reference Manual Rev. 1.0, May 1990.

21.0 ATTACHMENTS/APPENDICES

See attached pages.

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

Mercury Atomic Absorption
For the Analysis of Solid or Semisolid Waste
Automated Cold-Vapor Technique

UNCONTROLLED DOCUMENT

METHOD 7471A

APPROVALS:

Metals Supervisor: Betty C Doyle Date: 1/30/96

QA/QC Supervisor: Date: 1-30-96

Laboratory Manager: Date: 1-30-96

Procedure Number: GR-01-109

Revision Number: 2.0 By: Betty Doyle Effective Date: 1/30/96

Total Number of Pages: 41 Pages Revised: All

Subject:	Mercury Atomic Absorption For the Analysis of Solid or Semisolid Waste Automated Cold-Vapor Technique	Procedure No: GR-01-109 Revision No: 2.0 Effective Date: 1/30/96
	USEPA Method 7471	Page 1 of 41

1.0 PRINCIPAL METHOD REFERENCE

1.1 U.S. Environmental Protection Agency. Mercury in Solid or Semi-solid Waste (Manual Cold Vapor Technique) Method 7471A, SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, Revision 1, September 1994

2.0 PARAMETER LIST

Hg

3.0 SCOPE AND APPLICATION

Method 7471 is used for the determination of total mercury (inorganic and organic) in soil, sludge, oil, hazardous waste. All samples analyzed by this method must undergo a dissolution procedure to destroy any organic substances in the sample.

4.0 SUMMARY OF TEST METHOD

Prior to analysis, all samples, standards, and quality control samples must be prepared according to the procedure discussed in Section 12 of this method. This digestion procedure breaks down organo-mercury compounds into inorganic mercury. The inorganic mercury is then converted to the Hg^{+2} state for subsequent analysis.

The prepared liquid sample with mercury in the divalent form (Hg^{+2}) enters the mercury analysis system and is mixed with stannous sulfate to form elemental mercury vapor (Hg^0) according to the following equation:

$$Hg^{+2} + Sn^{+2} \text{-------}> Hg^0 + Sn^{+4}$$

The mixture flows into a liquid-gas separator where argon is introduced to carry the mercury through a drying tube containing magnesium perchlorate. The dry mercury vapor then enters one path of a heated double-path optical cell which has been optimized for fast response time. A mercury source powered by a constant current power supply delivers a stable source of emission at 253.7 nm. Absorbance by the mercury vapor is measured

using a solid state detector with a wide dynamic range. The resulting signal is referenced to the simultaneous absorbance of the pure carrier gas flowing through the second optical path under identical conditions. The absorbances of the standards are plotted against the known concentrations. Absorbance readings from unknown samples are then read from the standard curve and extrapolated to the concentration. The mercury vapor is then passed through activated carbon prior to being vented up a hood to reduce the mercury emissions from this test.

5.0 INTERFERENCES AND CORRECTIVE PROCEDURES

5.1 Soil samples often contain mercury at low levels. The preparation area must be kept free of dust and dirt to avoid contamination.

5.2 Certain volatile organic materials that absorb at this wavelength (253.7 nm) may also cause interference. If an interference is suspected, a preliminary run without reagents should determine if this type of interference is present.

5.3 The inorganic lab uses a product called Chrom-merge which contains mercury at fairly high concentrations to clean BOD bottles. Since this method uses the same type of bottles as the BOD test, the analyst should ensure that the bottles used for this test are 'Metals' bottles and that they have not been washed with the reagent. All BOD bottles used for mercury have an 'M' etched on the side of the bottle. If the bottles have been contaminated with the reagent, all suspected bottles must be thoroughly washed before use.

5.4 If a thermometer is broken anywhere in the laboratory, the metals lab will be notified. The possibility exists that sample bottles may become contaminated from the mercury vapor from the broken thermometer. If contamination is suspected, the contents of the bottles must be disposed of and the samples redigested.

5.5 Mercury may be lost from samples during drying if the temperature of the oven exceeds 60°C. All solid samples must be dried at 60°C and homogenized prior to digestion.

5.6 Mercury may be lost if the temperature of the water bath used to perform the digestion goes above 95°C. All water baths used for digestion must have their temperature

monitored with an alcohol thermometer. The temperature of the water bath must be recorded in the mercury digestion logbook.

5.7 The reagents used in this procedure may become contaminated over time. If contamination is suspected, the reagent must be discarded and fresh reagent made.

6.0 SAFETY PRECAUTIONS

6.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the "TriMatrix Laboratory Safety Manual".

6.2 Concentrated acids are used in the preparation of standards and samples for analysis by cold vapor. Gloves and safety glasses must be worn at all times when handling concentrated acids. Gloves must also be worn when handling digested samples. Please refer to the MSDSs for information on these or any other chemicals utilized in this procedure.

6.3 Check the exhaust hood over the instrument to be sure it is operating correctly. If the ventilation system is not working properly, immediately contact the metals lab supervisor. Under no circumstances should the cold vapor unit be used if the exhaust hood is not working.

6.4 UV protective glasses must be worn at all times in the metals laboratory. The mercury lamp emits UV radiation. Avoid looking directly at the lamp without some type of strong UV protection. Failure to follow this policy may cause very serious and immediate damage to the retina of the eye.

6.5 The cold vapor unit uses Argon (Ar) as the carrier gas for the mercury vapor. Although Ar in and of itself is neither hazardous nor flammable, it may cause suffocation through oxygen deprivation. It is therefore imperative that all sources of Ar be turned off with a valve when not in use. Since Ar is colorless and odorless, if you feel lightheaded, please evacuate the metals lab at once and notify the metals lab supervisor. Please refer to the MSDSs for information on this or any other chemicals utilized in this procedure.

6.6 Mercury may exist in many forms, and is toxic in a variety of ways. Mercury vapor is toxic if inhaled. Do not operate the instrument if it is not properly ventilated. Hg^{+2} is toxic if ingested. Always wash hands after handling the mercury standard.

6.7 Many of the reagents used in this procedure are toxic if ingested. Please refer to the MSDSs for information on the chemicals utilized in this procedure.

6.8 No food or drink is allowed in the metals lab. Food or drink may become contaminated with acid or metals and may therefore be hazardous.

6.9 Wash hands before starting work. Chemicals may be present on the skin which may interfere with metals analysis. Wash hands before leaving the metals lab. Chemicals and acids may be on the skin which could eventually be ingested or passed on to a third party through casual contact.

7.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

7.1 All sample containers must be pre-washed with detergents, acids and ASTM Type II water. Plastic and glass containers are both suitable, although glass is preferable since mercury may be adsorbed by certain plastics.

7.2 No preservation is required for solid or semi-solid samples. All samples should be refrigerated until there is time to dry the samples and prepare them for analysis.

7.3 For solids or semi-solids, moisture must be driven off in a drying oven at a temperature of $60^{o}C$.

7.4 All samples must be subjected to a dissolution step prior to analysis. For specific steps see Section 10 of this method.

8.0 APPARATUS/INSTRUMENTATION

8.1 300 ml BOD bottles. The bottles must be in good condition and have a ground-glass stopper. If the bottles are weak in any way, they will crack when subjected to the preparation procedure.

8.2 Laboratory analytical balance capable of weighing 0.1 mg.

8.3 Laboratory balance capable of weighing 0.1 g.

8.4 Plastic weigh boats. The weigh boats used must be free of mercury. Usually, the weigh boats are used to weigh the samples and dispense the sample into the BOD bottle. In the case of oil samples and some wastes, the weigh boat is actually placed in the BOD bottle with the sample to reduce weighing errors.

8.5 Eppendorf pipettors capable of delivering 50-1000 µl.

8.6 Class A volumetric flasks, various volumes.

8.7 Class A reusable pipettes, various volumes.

8.8 Oxford pipettes capable of dispensing 5 to 10 mls of solution.

8.9 Hotplates capable of heating water to 95°C and maintaining the temperature of the water at 95°C.

8.10 Roasting pans with lids. The pans must be capable of holding water. The lids should fit securely over the pan, but should not be air-tight.

8.11 Magnetic stir plate and stirbar.

8.12 Laboratory spatulas. The spatulas must be cleaned prior to use.

8.13 Timer capable of counting down from 30 minutes.

8.14 Glass alcohol thermometer. Mercury thermometers must never be used in this procedure. The thermometer must be readable at 95°C.

8.15 Leeman Labs PS200 automated mercury system. The instrument has an attached autosampler that is capable of aspirating sample and reagents. A regulator is built into the instrument to deliver the Ar to the sample stream. The instrument is a double-beam instrument capable of measuring the change in intensity of a mercury lamp at 253.7 nm. The Ar used to purge the mercury vapor from the sample is used as the reference beam. To compensate for any aberrations in the optical path, the instrument has an adjustment screw to tune the path so that they react the same to the emission of the mercury lamp.

8.16 Computer running Leeman PS 200 control software. An IBM compatible 80386SX16 or better computer with at least 1 MB RAM, a 40 MB hard disk, and a VGA color monitor is needed. The current software used by the instrument is PS200 version 2.008. The software version may be updated without notice if it performs at least as well as the older version. Major updates to the software that require the analyst to deviate from the stated procedure will require an update to this SOP.

8.17 Epson printer or equivalent. The specific printer used must respond to Epson printing codes. The printer must be attached to the computer using an appropriate communication cable. Please refer to the Instrument manual for further printer specifications.

9.0 ROUTINE PREVENTIVE MAINTENANCE

9.1 Check calibration on pipettors prior to use. Please refer to the Eppendorf pipettor SOP for calibration procedures and corrective actions.

9.2 Verify calibration of the balance. Please refer to the balance SOP for calibration procedures and corrective actions.

9.3 Inspect the Ar supply when the shift begins. If the liquid level of the Ar falls below the reorder mark, notify the person responsible for ordering gasses or the metals supervisor.

9.4 Inspect the waste container on the floor under the instrument every shift. If the jug is full, properly dispose of the liquid.

9.5 Inspect the printing quality of the printer. If the print is hard to read or light in appearance, replace the printer cartridge with the appropriate replacement.

9.6 Check all tubing for flattened areas, leaks, and clogs before use. If any problems are found, change the tubing and note the change in the instrument maintenance logbook.

9.7 Prior to analysis, rinse the entire system with 1:3 HCl for about ½ hour followed by ASTM Type II H_2O for another ½ hour.

9.8 The aperture must be checked before the analysis has begun. See the analytical method for a discussion on how the aperture is tested.

9.9 The instrument must be given the appropriate amount of time to warm up before use. If the instrument has been shut down in 'Ovemite' mode, it is highly recommended that the 'WARMSTRT' macro be invoked to warm the instrument up. If the instrument has been shut down for an extended period of time, the 'COLDSTRT' macro should be used.

9.9.1 The WARMSTRT macro asks a series of questions to the user to ensure that everything is in place and is in working order. The instrument then warms up for 20 minutes to condition the tubing and stabilize the lamp. When answering the questions, if the user enters an invalid response, the macro will not continue. For example, one of the questions is 'Is the lamp on? <Y/N>'. If the user enters anything but 'Y', the macro will not continue. When the macro has completed the warm-up period, the message 'System Ready' is displayed on the screen. If the macro was called from another macro, such as the MERCURY macro, then control is given back to the calling macro and the calling macro will resume at the step after the call to the macro.

9.9.2 The COLDSTRT macro is similar to the WARMSTRT macro, but the warm-up period is much longer since it will be invoked only if the instrument has been shut

down for an extended period of time. Again, the questions are programmed such that only certain responses will allow the macro to continue. The warm up time for this macro is 2½ hours. When the macro has completed the warm-up period, the message 'Operation Complete' is displayed on the screen. If the macro was called from another macro, such as the MERCURY macro, then control is given back to the calling macro and the calling macro will resume at the step after the call to the macro.

10.0 CHEMICALS AND REAGENTS

10.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Redistilled acids may be used if it has been demonstrated that the acid is free from contamination.

10.1.1 Concentrated hydrochloric acid, trace metal grade.

10.1.2 Concentrated nitric acid, trace metal grade.

10.1.3 Concentrated sulfuric acid, trace metals grade.

10.2 **ASTM Type II water** (ASTM D1193). Deionized water is fed into an all glass distillation unit. The resulting distillate is immediately placed into a plastic container. Impurities are measured by the Inorganic group at TriMatrix. This is the only water acceptable for use in the Metals lab for dilutions or standard preparation.

10.3 **Standard stock solutions** are purchased primarily from Inorganic Ventures. All stock solutions are ICP grade single-element solutions at concentrations of 1000 or 10000 ppm.

10.4 Argon gas supply: Welding grade or better. Currently, this is plumbed from a liquid Ar tank located outside of the building. Ar is used as the carrier gas for analysis.

10.5 Aqua Regia: Prepare immediately before use in a hood by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3. This solution should be

constantly stirred during use on low speed to reduce the amount of gas that the pipettor picks up. **CAUTION:** Chlorine gas is constantly liberated from this solution. The solution may only be used under a hood. If chlorine is detected outside of the hood, try to correct the problem by checking all sample bottles.

10.6 Sulfuric Acid 0.5N. Rinse a clean 1 liter volumetric flask several times with ASTM Type II water. Place about 500 ml ASTM Type II water in the flask. Carefully add 14 ml concentrated sulfuric acid to the water. Carefully swirl the flask to mix the solution. Dilute to the mark with ASTM Type II water. **Note:** the addition of H_2SO_4 to water will cause a considerable amount of heat to be generated. Mix well.

10.7 Potassium Permanganate, 5% solution (W/V). In a plastic 3-liter container, place 150 g $KMnO_4$ crystals. Add 3 L ASTM Type II water to the container. Place a stirbar in the solution and stir on a stirplate until all of the crystals have dissolved. Since this solution is nearly a saturated solution, it may take several hours to prepare. To check if the crystals have dissolved, a glass pipette may be used to probe the bottom of the container for excess crystals. If any of the solution is spilled, immediately clean up the spill with water. If a brownish stain remains, it may be removed from surfaces with hydroxylamine hydrochloride. If the solution touches exposed skin, the skin will turn brown. The brown discoloration is not harmful as long as the excess permanganate is washed off. The stain will wear off over time. Potassium permanganate will collect mercury if left exposed to the atmosphere. The container must be covered when not in use and should be stored in a dark cabinet to reduce the potential for auto-catalytic reduction.

10.8 Sodium Chloride Hydroxylamine Hydrochloride, 12% solution (W/V). In a plastic 3-liter container, place 360 g of sodium chloride and 360 g of hydroxylamine hydrochloride. Add 3 L of ASTM Type II water and a stirbar. Place the container on a stirplate and stir until all of the crystals have dissolved.

10.9 Stannous Sulfate, 10% solution (W/V). Rinse a clean 500 ml volumetric flask several times with ASTM Type II water. Place about 250 ml 0.5 N H_2SO_4 in the flask. Add 50 g stannous sulfate and dilute the flask to volume with 0.5 N H_2SO_4. Mix well. When the crystals have gone into solution, filter through a 0.45 µm filter by using a vacuum apparatus and a side arm filtering flask. **NOTE:** This mixture is a suspension and must be stirred continuously during use, even after filtration.

11.0 STANDARDS

11.1 All standards are single-element standards. All standards are good for 1 day.

11.2 Preparation of the 10,000 ppb standard.

11.2.1 Rinse a clean 100 ml volumetric flask with ASTM Type II water several times.

11.2.2 Place about 20 ml of ASTM Type II water in the flask.

11.2.3 Add 0.5 ml concentrated trace metal grade HNO_3 to the flask and swirl.

11.2.4 Pipette 1 ml 1000 ppm stock standard solution into the volumetric flask.

11.2.5 Dilute the flask to the mark and mix well.

11.2.6 Update the stock standard logbook.

11.2.7 Transfer the standard number from the standard logbook to the volumetric flask.

11.3 Preparation of the 1000 ppb standard.

11.3.1 Rinse a clean 100 ml volumetric flask with ASTM Type II water several times.

11.3.2 Place about 20 ml of ASTM Type II water in the flask.

11.3.3 Add 0.5 ml concentrated trace metal grade HNO_3 to the flask and swirl.

11.3.4 Pipette 10 ml 10,000 ppb stock standard solution prepared in Step 11.2 into the volumetric flask.

11.3.5 Dilute the flask to the mark and mix well.

11.3.6 Update the stock standard logbook.

11.3.7 Transfer the standard number from the standard logbook to the volumetric flask.

11.4 Preparation of the 100 ppb standard.

11.4.1 Rinse a clean 100 ml volumetric flask with ASTM Type II water several times.

11.4.2 Place about 20 ml of ASTM Type II water in the flask.

11.4.3 Add 0.5 ml concentrated trace metal grade HNO_3 to the flask and swirl.

11.4.4 Pipette 1 ml 10,000 ppb stock standard solution prepared in Step 11.2 into the volumetric flask.

11.4.5 Dilute the flask to the mark and mix well.

11.4.6 Update the stock standard logbook.

11.4.7 Transfer the standard number from the standard logbook to the volumetric flask.

11.5 Preparation of working standards.

11.5.1 Set aside 12 clean BOD bottles for the mercury working curve.

11.5.2 Label the BOD bottles as follows:

5.0 ppb ---------- 2 bottles
2.0 ppb ---------- 2 bottles
1.0 ppb ---------- 2 bottles
0.5 ppb ---------- 2 bottles
0.2 ppb ---------- 2 bottles
Blank ---------- 2 bottles

11.5.3 Pipet 5 ml of the 100 µg/L Hg standard into each of the BOD bottles labeled 5.0 ppb. Add 5 ml ASTM Type II water to give a final volume of 10 ml in each BOD bottle.

11.5.4 Pipet 2 ml of the 100 µg/L Hg standard into each of the BOD bottles labeled 2.0 ppb. Add 8 ml ASTM Type II water to give a final volume of 10 ml in each BOD bottle.

11.5.5 Pipet 1 ml of the 100 µg/L Hg standard into each of the BOD bottles labeled 1.0 ppb. Add 9 ml ASTM Type II water to give a final volume of 10 ml in each BOD bottle.

11.5.6 Using a calibrated Eppendorf pipette, pipet 0.5 ml of the 100 µg/L Hg standard into each of the BOD bottles labeled 0.5 ppb. Add 9.5 ml ASTM Type II water to give a final volume of 10 ml in each BOD bottle.

11.5.7 Using a calibrated Eppendorf pipette, pipet 0.1 ml of the 100 µg/L Hg standard into each of the BOD bottles labeled 0.1 ppb. Add 9.9 ml ASTM Type II water to give a final volume of 10 ml in each BOD bottle.

11.5.8 Add 10 ml ASTM Type II water to each of the BOD bottles labeled Blank.

11.5.9 All working standards must be digested within 8 hours of preparation.

11.5.10 Complete the standards log book. See Appendix J.

11.6 Preparation of the Laboratory Fortified Blank (LFB).

11.6.1 Label 2 clean BOD bottles as LFB.

11.6.2 Add 10 ml ASTM Type II to each of the bottles labeled LFB.

11.6.3 Using a calibrated Eppendorf pipette, pipet 0.25 ml of the 1000 µg/L Hg standard into each of the BOD bottles labeled LFB.

11.7 Preparation of the Laboratory Control Sample (LCS).

11.7.1 Label 2 clean BOD bottles as LCS.

11.7.2 Add 10 ml ASTM Type II to each of the bottles labeled LCS.

11.7.3 Pipette 1 ml of the 3 ppm concentrated LCS sample (SP1035) obtained from SPEX into each of the bottles labeled LCS. Note: a concentrated LCS from another vendor or of another concentration may be substituted for the above LCS, as long as the LCS is from a different source than the primary standards and the final concentration of the diluted LCS is around the midpoint of the calibration curve.

12.0 SAMPLE PREPARATION

12.1 Solid sample Preparation

12.1.1 Weigh triplicate 0.2g portions of untreated sample into BOD bottles ~~All samples must be prepared in triplicate. Matrix spikes and matrix spike duplicates must also be prepared in triplicate.~~ DWJ 7-10-97

12.1.2 All soils, sludges, and sediments must be dried and homogenized prior to digestion by this method. See Appendix M for a discussion on drying and crushing soils.

12.1.3 Wastes, liquid wastes, oils, solvents, TCLP oil phases, and other non-soil sample types are analyzed as-is after homogenization. Weigh triplicate 0.1g portions into BOD bottles DWJ 7-10-97

12.1.4 Generate a worklist for mercury digestion from LIMS. See Appendix F.

12.1.5 Label 1 BOD bottles with the sample number. If the sample will have matrix QC performed on it, then label 2 additional BOD bottles, 1 as the sample SPK, and 1 as the sample MSD. Make sure that the sample number is located somewhere on SPK and MSD bottles.

12.1.6 Weigh out the sample

12.1.6.1 For waste or sludge samples, weigh ~~0.100 g~~ triplicate 0.1g portions of sample in a plastic weigh boat. Transfer the sample to the BOD bottle. If the sample has obviously adhered to the weigh boat, push the weigh boat into the bottle with the sample. Label the bottle with the sample number and the dilution factor ~~(X1000)~~ DWT 7-10-97

12.1.6.2 For soil or soil-like samples, weigh ~~0.200 g~~ triplicate 0.2g portions of sample in a plastic weigh boat. Transfer the sample to the BOD bottle. If the sample has obviously adhered to the weigh boat, push the weigh boat into the bottle with the sample. Label the bottle with the sample number and the dilution factor ~~(X500)~~ DWT 7-10-97

12.1.7 Repeat Step 12.1.6 for the remaining bottles for the sample. Discard the weigh boat when the sample is finished.

12.1.8 Repeat Steps 12.1.5 and 12.1.6 for the remaining samples in the digestion batch.

12.1.9 Add ~~5~~ 10 ml ASTM Type II water to each sample bottle. DWT 7-10-97

12.1.10 In a fume hood, add 5 ml aqua regia to each bottle.

12.1.11 Plunge the bottles into a water bath that is maintained at 95°C. Cook the samples for 2 minutes. The temperature of the water bath must be monitored using a thermometer. Note the temperature of the water bath in the mercury digestion logbook.

NOTE: If any of the bottles have been weakened, the bottoms may fall off the bottle. If the bottle breaks, immediately prepare another bottle of the sample.

12.1.12 Cool the samples on the counter until cool or warm to the touch.

12.1.13 Add 50 ml ASTM Type II water to each bottle. Mix well by swirling the bottle after the addition.

12.1.14 Add 15 ml of the 5% potassium permanganate solution to each bottle. Mix well by swirling the bottle after the addition.

12.1.15 Plunge the bottles into a water bath that is maintained at 95°C. Cook the samples for 30 minutes. The temperature of the water bath must be monitored using a thermometer. Note the temperature of the water bath in the mercury digestion logbook

NOTE: If any of the bottles have been weakened, the bottoms may fall off the bottle. If the bottle breaks, immediately prepare another bottle of the sample.

12.1.16 Cool the samples on the counter until cool or warm to the touch.

12.1.17 In a fume hood, add 6 ml of the 12% hydroxylamine hydrochloride solution to each bottle. Mix well by swirling the bottle after the addition.

NOTE: The addition in 12.1.17 will generate large quantities of N_2 gas. Since there is Cl_2 gas in the headspace of the bottle, the liberation of N_2 will push the Cl_2 out of the bottle. Therefore, this addition must be done in a hood. For some samples, the effervescence may become quite vigorous and the stopper may be blown off the BOD bottle.

12.1.18 While the samples are still in the fume hood, add 50 ml ASTM Type II water to each bottle. Mix well by swirling the bottle after the addition. DWS 7-10-97

12.1.19 Arrange the bottles on the counter so that the three bottles for each sample are next to each other.

12.1.20 Print out a LIMS pretreatment benchsheet. See Appendix F.

12.1.21 Pretreat the samples on LIMS. See Appendix C.

12.1.22 Fill out the mercury digestion logbook. See Appendix D.

12.2 Working standard Preparation

12.2.1 Prepare the working standards as described in Section 11.5.

12.2.2 Prepare an LCS for the analysis by pipetting an appropriate amount of a concentrated LCS solution into a BOD bottle so that the final concentration of the LCS is about equal to the midpoint of the calibration curve. When calculating the amount of spike needed, use 100 ml for the final volume.

12.2.3 In a fume hood, add 5 ml aqua regia to each bottle of standard and LCS.

12.2.4 Plunge the bottles into a water bath that is maintained at 95°C. Cook the standards for 2 minutes. The temperature of the water bath must be monitored using a thermometer. Note the temperature of the water bath in the mercury digestion logbook.

NOTE: If any of the bottles have been weakened, the bottoms may fall off the bottle. If the bottle breaks, immediately prepare another bottle of the standard or LCS.

12.2.5 Cool the standards and LCS on the counter until cool or warm to the touch.

12.2.6 Add 50 ml ASTM Type II water to each bottle. Mix well by swirling the bottle after the addition.

12.2.7 Add 15 ml of the 5% potassium permanganate solution to each bottle. Mix well by swirling the bottle after the addition.

12.2.8 Plunge the bottles into a water bath that is maintained at 95°C. Cook the standards and LCS for 30 minutes. The temperature of the water bath must be monitored using a thermometer. Note the temperature of the water bath in the mercury digestion logbook.

NOTE: If any of the bottles have been weakened, the bottoms may fall off the bottle. If the bottle breaks, immediately prepare another bottle of the sample.

12.2.9 Cool the standards and LCS on the counter until cool or warm to the touch.

12.2.10 In a fume hood, add 6 ml of the 12% hydroxylamine hydrochloride solution to each bottle. Mix well by swirling the bottle after the addition.

NOTE: The addition in 12.2.9 will generate large quantities of N_2 gas. Since there is Cl_2 gas in the headspace of the bottle, the liberation of N_2 will push the Cl_2 out of the bottle. Therefore, this addition must be done in a hood. For some samples, the effervescence may become quite vigorous and the stopper may be blown off the BOD bottle.

12.2.11 While the standards and LCS are still in the fume hood, add 50 ml ASTM Type II water to each bottle. Mix well by swirling the bottle after the addition.

12.2.12 Fill out the mercury digestion logbook. See Appendix D.

13.0 CALIBRATION PROCEDURES (INSTRUMENTAL ANALYSIS)

13.1 Calibration of the instrument must be performed every 24 hours or for every batch of samples that were prepared in the same manner, whichever is more frequent. For example, if a soil calibration was performed at 8 AM and a water run is to be performed at 5 PM of the same day, a new calibration curve must be performed with standards prepared with the samples to be analyzed.

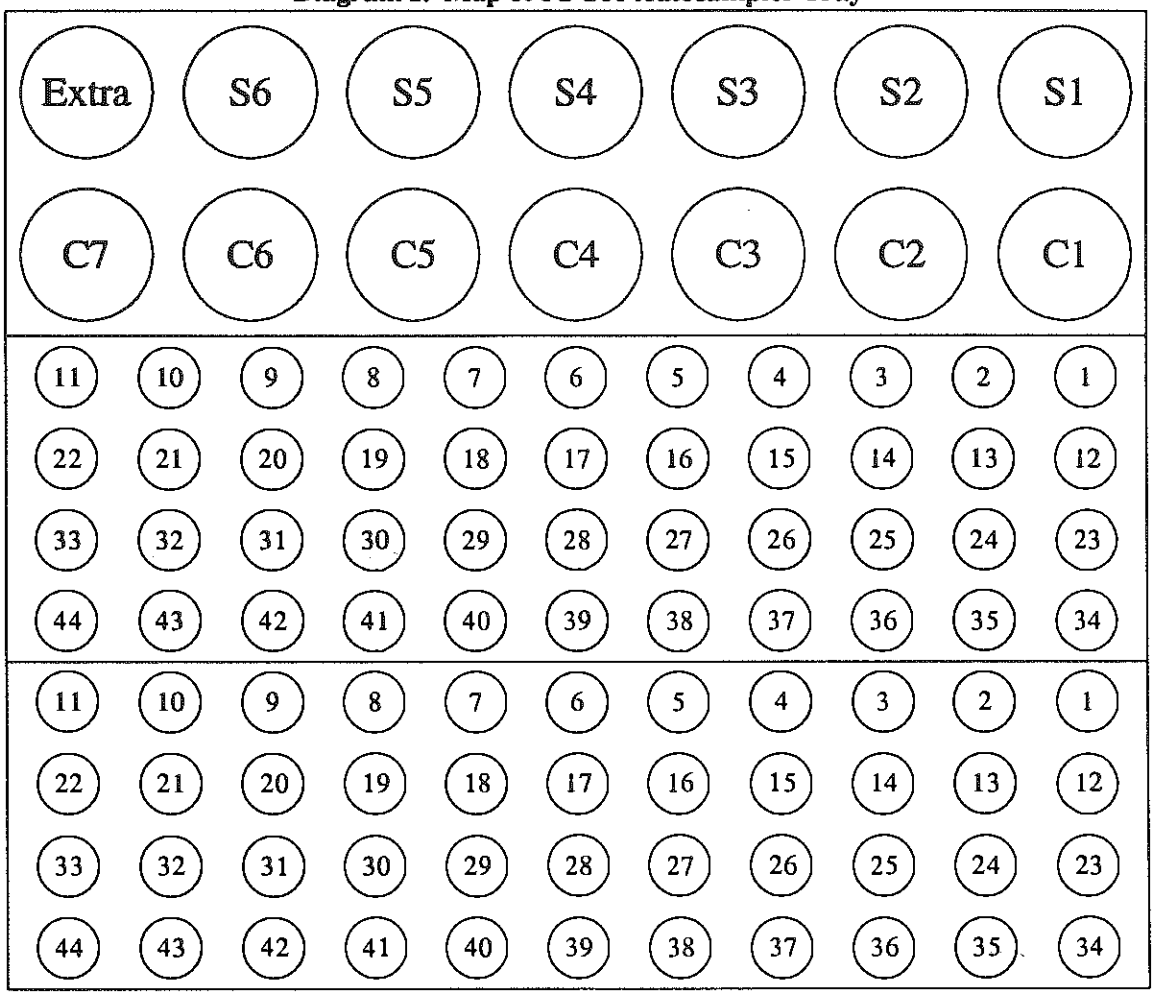
13.2 Start the instrument software as described in Section 14. Perform a COLDSTRT or a WARMSTRT, whichever is appropriate.

13.3 Load the autosampler tray with the appropriate standards. See Table 1 for autosampler positions. Rack 0 is the rack that is furthest away from the front of the instrument. See Diagram 1 for autosampler position designation.

Table 1. Autosampler Positions for Standards

Autosampler Position	Standard Concentration (ppb)
Rack 0, Position 1 (S1)	0 (Blank)
Rack 0, Position 2 (S2)	0.1
Rack 0, Position 3 (S3)	0.5
Rack 0, Position 4 (S4)	1.0
Rack 0, Position 5 (S5)	2.0
Rack 0, Position 6 (S6)	5.0

Diagram 1. Map of PS-200 Autosampler Tray



13.4 There are currently three ways to calibrate the instrument. Although the three methods are different in the keystrokes used, they are essentially performing the same task.

13.4.1 Method 1: Allow the MERCURY macro to run the standards unattended. This method will automatically initialize all parameters, run the standards, check the QC, run samples, and run periodic QC.

13.4.1.1 Start the MERCURY macro. When the PS200 software is booted up, the MERCURY macro is automatically invoked. If, for some reason the macro is stopped, the macro can be restarted by pressing <F2> then typing in MERCURY and pressing <Enter>.

13.4.1.2 Follow the direction outlined in Section 14 until the software asks if standards should be ran. Answer 'Y' to this question.

13.4.1.3 The instrument will automatically run the standards and plot the calibration curve when finished. Skip to Step 13.5.

13.4.2 Method 2: Use the RUNSTDS macro to run the standards unattended. This method will run the standards unattended and then stop. The user will have to either invoke the MERCURY macro again to restart the analysis in unattended mode or else the run will have to be performed manually.

13.4.2.1 Set up the instrument as described in Section 14. Perform a WARMSTRT or a COLDSTRT, if needed.

13.4.2.2 Start the macro by pressing <F2>, then typing in RUNSTDS and pressing <Enter>.

13.4.2.3 The instrument will automatically run the standards and plot the calibration curve when finished. Skip to Step 13.5.

13.4.3 Method 3: Run each standard individually. This method needs constant operator attendance and should not be used if the entire curve is to be ran. The operator is responsible for checking all values before running the analysis if this method is used.

13.4.3.1 Press <F6> (Standard).

13.4.3.2 The software will ask for the standard number to run. Enter the standard number that should be analyzed. Do not enter the standard concentration,

only the standard position. Refer to Diagram 1 for the standard autosampler position.

13.4.3.3 Repeat steps 13.4.3.1 and 13.4.3.2 for the remaining standards that need to be ran.

13.4.3.4 When finished running the standards, go to the calibration page by pressing <F1> (Main Menu) then pressing <C> (Calibration) <L> (Line calibration). At this point a plot of the calibration should be displayed.

13.4.3.5 Press <A> to accept the calibration curve.

13.5 The correlation coefficient 'r' must be equal to or greater than 0.995. If the correlation coefficient is not equal to or greater than 0.995, you may edit the calibration curve.

13.5.1 Rerun a point in the calibration curve.

13.5.1.1 Press <F6> (Standard).

13.5.1.2 The software will ask for the standard number to run. Enter the standard number that should be analyzed. Do not enter the standard concentration, only the standard position. Refer to Diagram 1 for the standard autosampler position.

13.5.1.3 Repeat steps 13.5.1.1 and 13.5.1.2 for the remaining standards that need to be ran. **NOTE:** The software will not automatically re-calculate the correlation coefficient. The user must press <A> to re-calculate the coefficient.

13.5.2 Delete a point in the curve that is not correct. Since it is possible that there was a determinate error in the preparation of the standards, standard points may be dropped if they appear to significantly deviate from the curve. At least 3 standards, one of which is the lowest standard of the

curve, and the blank must remain in the curve for the calibration curve to be valid.

13.5.2.1 Use the arrow keys to highlight the point that is to be deleted from the curve.

13.5.2.2 Press <Enter> to delete the point from the calibration curve.

13.5.2.3 Press <A> to re-calculate the calibration curve and correlation coefficient.

13.5.3 Add a previously deleted point back to the curve. If a calibration point has been deleted by accident, or if it was deleted to check its affect on the remaining curve, the point may be added back without re-running the point. At least 3 standards, one of which is the lowest standard of the curve, and the blank must remain in the curve for the calibration curve to be valid.

13.5.3.1 Use the arrow keys to highlight the point that is to be added back to the curve.

13.5.3.2 Press <Enter> to add the point to the calibration curve.

13.5.3.3 Press <A> to re-calculate the calibration curve and correlation coefficient.

13.6 If the MERCURY macro was used to produce the analytical curve, press <F2> when the curve is acceptable. The software will double check that the correlation coefficient is correct, then print the analytical curve if the correlation is acceptable. The macro will then automatically start analyzing the quality control samples and samples. See Section 14 for a more in depth discussion on performing the analysis.

13.7 If the RUNSTDS macro was used to produce the analytical curve, press <F2> when the curve is acceptable. The software will double check that the correlation coefficient is correct, then print the analytical curve if the correlation is acceptable. The macro will then end. At this point, the quality control samples must be analyzed. If an unattended mode of operation is preferred, start the MERCURY macro by pressing <F2> and then typing in MERCURY<Enter>. Performing the analysis manually is beyond the scope of this procedure. See Section 14 for a more in depth discussion on performing the analysis.

13.8 If the curve was constructed by manually running the standards, double check that the curve is accepted the curve by pressing <A>. Check to ensure that the correlation coefficient is still 0.995 or greater. If the correlation is not at least 0.995, go back to step 13.5 and edit the calibration. If the correlation is okay, print the curve by pressing <F4> (Print Screen). At this point, the quality control samples must be analyzed. If an unattended mode of operation is preferred, start the MERCURY macro by pressing <F2> and then typing in MERCURY<Enter>. Performing the analysis manually is beyond the scope of this procedure. See Section 14 for a more in-depth discussion on performing the analysis.

14.0 ANALYTICAL PROCEDURE

14.1 This procedure assumes that the user has been introduced to the software either by reading the software manual or by experienced metals personnel. Advanced topics, such as how to replace the mercury source lamp are beyond the scope of this method. In this case, the user should reference the instrument manual.

14.2 Make sure that the argon supply is on. There is a valve behind the instrument that supplies the PS200 instrument. Make sure that the valve is open.

14.3 Turn the instrument on if it is not already on. The power button for the instrument is the blue button on the front of the instrument. If the instrument fails to turn on, contact the metals lab supervisor.

14.4 Turn the computer and printer on if they are not turned on. If the computer fails to boot, contact the metals lab supervisor.

14.5 Turn the lamp on. The lamp power button is the green button on the front of the instrument. Allow the lamp to warm up for at least ½ hour before testing the aperture. If the lamp does not seem to be working, contact the metals lab supervisor.

14.6 The computer will automatically start the MERCURY macro. Stop the macro by pressing <F10> (Stop).

14.7 Place the stannous sulfate line (the line connected to the red/red tubing) and the sample line (the line connected to the black Viton tubing) in the wash vessel. Fill the wash vessel with 10% HCl solution.

14.8 Check the peristaltic tubing. If the tubing is blocked or badly worn, replace it with new tubing.

14.9 Clamp the tubing in place. Make sure that the peristaltic tubing is in a straight line over the pump rollers. Lift the red lever on the pump manifold to press the tubing against the rollers.

14.10 Start the pump. From the **Main Menu** , go to the **Instrument** screen by pressing **I**. Press **O** to go to the **Operation** screen. Press **R** then **O** to start the pump.

14.11 Turn on the Argon carrier gas. While in the **Instrument Operation** screen, press **G** then **O** to turn on the carrier gas.

14.12 Check the peristaltic tubing to ensure that the pump is drawing liquid. Lift the sample line out of the rinse solution to see if the pump will pull air. Check the stannous sulfate line the same way. Watch the drain line right after the liquid/gas separator to see if bubbles are being drawn through the tubing. If none of the tubing is drawing, make sure that the pump is turning. If a single piece of tubing is not drawing, try to increase the tension to make the tubing draw by lifting the red lever on the pump manifold higher. If liquid is still not being drawn, try changing the tubing (See Section 9.6). If the pump still does not draw, a clog

should be suspected. Please see the metals lab supervisor for help in finding and correcting the cause of the clog.

14.13 Fill the drying tube with drying agent. Currently, the metals lab is using Magnesium Perchlorate (Anhydrone) as the drying agent for mercury determinations.

14.13.1 Place a small amount of glass wool in one end of the drying tube. There should be just enough glass wool to keep the drying agent from falling out of the tube. Do not put too much glass wool in the end of the tube as this may restrict gas flow through the drying tube.

14.13.2 While wearing gloves, carefully fill the drying tube with fresh magnesium perchlorate. Fill the tube up to the neck of the tube. Gently tap the bottom of the tube on the counter to help the crystals settle into place. Do not over pack the tube as this will restrict the gas flow through the tube. Fill the tube up again within ¾ inch of the end of the tube.

14.13.3 Place a small amount of glass wool in the end of the drying tube. There should be just enough glass wool to keep the drying agent from falling out of the tube. Do not put too much glass wool in the end of the tube as this may restrict gas flow through the drying tube.

14.13.4 Check the O-rings on the drying tube endcaps for wear. Replace these O-rings if there is obvious wear.

14.13.5 Place the drying tube end caps on the end of the drying tube. Push the ends on until they stop. Tighten the nut on the endcaps until snug. Do not over tighten the endcaps.

14.13.6 Place the drying tube in its holder on the instrument.

14.14 If the lamp has been on for at least ½ hour, test the aperture.

14.14.1 Start the APERTEST macro.

14.14.1.1 Press <F2> (Macro).

14.14.1.2 Type in APERTEST, then press <Enter>.

14.14.2 The macro will now start to display some numbers on the screen. These numbers are the readings for the aperture and they represent the difference in intensity between the sample beam of the instrument and the reference beam.

14.14.3 The aperture reading must be 0±100, preferably 0±20. If the reading is not within specifications, adjust the aperture until the value is within range. Adjustment should be done as quickly as possible so that the temperature of the flow cell does not change significantly.

14.14.3.1 Remove the front cover from the instrument to reveal the flow cell. Push the cover up and then pull forward to remove.

14.14.3.2 Remove the Allen wrench from the front panel. The wrench is used to turn the aperture screws.

14.14.3.3 There are two screws on the flow cell at the right-hand end of the flow cell. Always adjust the screw that has been turned into the flow cell the furthest.

14.14.3.4 If the reading is negative, turn the screw clockwise until the reading is zero.
NOTE: In order to obtain an accurate reading, let go of the Allen wrench while taking the reading. Any pressure applied to the flow cell during the reading will change the reading.

14.14.3.5 If the reading is positive, turn the screw counter-clockwise until the reading is zero.

NOTE: In order to obtain an accurate reading, let go of the Allen wrench while taking the reading. Any pressure applied to the flow cell during the reading will change the reading.

14.14.3.6 Repeat steps 14.14.3.4 and 14.14.3.5 until the aperture reading is within the range 0±20.

14.14.3.7 Replace the Allen wrench in the front cover of the instrument.

14.14.3.8 Replace the front cover on the instrument. Make sure that the cover is seated firmly on the instrument and that the cover is flush with the instrument.

14.14.4 End the APERTEST macro by pressing <F8>. The macro will take one last reading of the aperture and print that value out on the printer.

14.15 Enter the sample identifications into the computer.

14.15.1 Go to the main menu by pressing <F1>.

14.15.2 Select the **Autosampler** screen by press A.

14.15.3 Enter the **Rack entry** screen by pressing R.

14.15.4 At the bottom of the screen, there will be a prompt for the rack name. The rack name is a combination of the month, day, analysis number of the day, and rack number of the analysis in a specific order. The format is:

MDDRA-N

Where:
M is the coded month
DD is the two digit date of the month

R is the letter R. It stands for Rack.

A is the numeric representation of the number of separate analyses that have been performed that day. An analysis is defined as a set of samples that are digested together. For example, if a water digestion is analyzed first thing in the day, then A would be 1. If a soil digestion is then analyzed during that day, A would be 2.

N is the numeric representation of the number of separate racks that have been performed for a given analysis for that day. For example, if a soil digestion has 5 racks, the first rack would have an N value of 1, the second a value of 2, the third a value of 3, and so on.

Type in the rack name in the space provided and press <Enter>. If the rack name does not exist, the computer will ask if it should create a new rack name. Answer 'Y' and press <Enter>. Place the rack name on the autosampler ID/WT sheet in the space provided.

14.15.5 Press the <Insert> key once to begin editing the contents of the rack.

14.15.6 The first column, labeled 'cup', contains the autosampler position number that corresponds to the ID/WT sheet used for setting up the autosampler tray. This field may not be edited.

14.15.7 The second column, labeled 'Id', will contain the sample identification that is located on the ID/WT sheet. The number or identification put in this column will be the LIMS sample number for the sample.

14.15.8 The third column, called 'Extended Id', while not commonly used, may be used to further identify the sample.

14.15.9 The third and fourth columns on the computer screen will contain the sample digestion weight and volume for the sample. For example, if 0.1 g of sample was digested, then the dilution factor would be 0.1 in the weight column and 100 in the volume column (0.1g was digested into 100 ml final solution). If a subsequent

dilution is performed on the sample, then the final volume is multiplied by that dilution factor. For example, if in the above example, the final solution is then diluted 10X, then the final volume would be 1000. Please see the metals lab supervisor for further instruction on this topic.

14.15.10 There are a total of 44 positions for each tray. To go down to the next page of autosampler positions, press <Page Down>. To go up to the previous page, press <Page Up>.

14.15.11 When the ID/WT sheet is completely entered into the computer for a rack, press 'E' to exit.

14.15.12 Repeat steps 14.15.4 through 14.15.11 for the remaining racks.

14.16 Start the MERCURY macro.

14.16.1 Press <F2> (Macro).

14.16.2 Type in MERCURY in the space provided, then press <Enter>.

14.17 At this point the MERCURY macro should start initializing the system. The macro will ask the user a series of questions to determine the state of the instrument. If the macro fails to start or if there are any problems from this point on, contact the metals lab supervisor.

14.18 The computer will ask 'Would you like to do a warm start? <Y/N>'. The warm start macro is used to prepare the PS200 for operation from the short-term shut down. If the lamp has been shut off for more than 1 hour, and the instrument has been left on, enter "Y". See Section 9.9 for a description of the WARMSTRT macro.

14.19 The macro will then ask the user 'Would you like to test the aperture? <Y/N>'. If the aperture has already been tested, answer 'N', otherwise answer 'Y'. For a discussion on the APERTEST macro, see Section 14.4.

14.20 A data file name must now be entered. The data file name must be unique, otherwise, the data will be appended to another data file. The data file name is a combination of the month, day of the month, and analysis number of the day. The format is:

MDDRA

Where:
M is the coded month
DD is the two digit date of the month
R is the letter R. It stands for Rack.
A is the numeric representation of the number of separate analyses that have been performed that day. An analyses is defined as a set of samples that are digested together. For example, if a water digestion is analyzed first thing in the day, then **A** would be 1. If a soil digestion is then analyzed during that day, **A** would be 2.

Type in the data name in the space provided and press <Enter>. If the data name does not exist, the computer will ask if it should create a new one. Answer 'Y' and press <Enter>. Place the data file name on the autosampler ID/WT sheet in the space provided.

14.21 The instrument will now prompt for the rack name and the autosampler positions that should be analyzed.

14.21.1 At the prompt 'Enter rack name (ENTER for none)', place the name of the first rack to be analyzed. If there is no rack, press the <Enter> key to skip this entry.

14.21.2 Type in the first autosampler position that is to be analyzed. Again, press <Enter> if there are no samples in the first physical rack to analyze.

14.21.3 Type in the last autosampler position to be analyzed on the first rack. Press <Enter> if there are no samples to analyze on the rack.

14.21.4 At the prompt 'Enter rack name (ENTER for none)', place the name of the second rack to be analyzed. If there is no rack, press the <Enter> key to skip this entry.

14.21.5 Type in the first autosampler position that is to be analyzed. Again, press <Enter> if there are no samples in the second physical rack to analyze.

14.21.6 Type in the last autosampler position to be analyzed on the second rack. Press <Enter> if there are no samples to analyze on the rack.

14.22 When the printer is done printing, the macro will take the user to the check sample screen. The user must verify that the values that the macro is putting in are okay. If the values entered for the BLK, the ICV/CCV, or the LCS are not correct, change them when prompted. If the values need to be updated in the macro, contact the metals lab supervisor.

14.23 The macro will now pause so that the user may check the values that have been entered automatically by the macro. This pause also allows the user to correct any mistakes that were made when entering data at the macro prompts. This SOP will not attempt to describe all of the information that may be edited. The user may refer to the instrument manual or may contact the metals lab supervisor if there is something that must be changed before beginning the analysis. When all of the values are okay, press <F2> to resume the macro.

14.24 As an added protection, the macro will ask 'Are you sure you want to start? <Y/N>'. Answer with the appropriate response. The macro will not continue until 'Y' is entered.

14.25 The computer will ask 'Do standards need running? <Y/N>'. The instrument must be calibrated every 24 hours or every time that a new digestion batch is started. Answer the question appropriately. If the standards do need to be ran, see Section 13 for a detailed explanation of the calibration sequence.

14.26 When the standards are complete, the instrument will automatically analyze the ICB. The ICB should read back within ± 0.1 µg/L. If at any point in the decision tree below the ICB is within the limits, the macro will jump to step 14.27.

14.26.1 If the ICB does not meet the criteria, the macro will ask the user to place a new vial of the blank in autosampler position C1. Press any key to continue.

Rf 8/2/99 If re-zero required, standards must also be run again. Rf 8/2/99

14.26.2 The instrument will then analyze the ICB again. If the ICB still does not meet the criteria, then the macro will autozero the instrument and rerun the ICB.

14.26.3 If the ICB does not read back within limits, the macro will essentially jump back to step 14.26.1. Please note that there is a possibility of an infinite loop occurring at this step. If the ICB refuses to work after 2 times through the decision tree, stop the macro and contact the metals lab supervisor for assistance.

14.27 When the ICB reads back within limits, the ICV will automatically be analyzed. The ICV is the midpoint calibration standard analyzed as a sample with the concentration being read from the analytical curve. The percent recovery for the ICV must be within the control limits of 90%-110% of the true value. If the ICV recovers within the control windows before the macro reslopes, then the macro will jump to Step 14.28.

14.27.1 If the ICV fails to recover within the control limits, the macro will ask the analyst to place a new vial of the ICV in autosampler position C2. When this is complete, press any key to continue the analysis.

re-sloping is no longer an option. Rf 8/2/99

~~14.27.2 If the ICV fails again, the macro will try to reslope the calibration based on an analysis of the midpoint standard. If the reslope fails, then the macro will rerun the standards and start again at Step 14.26.~~

~~14.27.3 If the reslope has a correlation coefficient greater than 0.995, then the macro will start again at Step 14.26.~~

14.28 The macro will now analyze an independent standard called the Laboratory Control Sample (LCS). The percent recovery must fall within the LIMS (Laboratory Information Management System) control limit for this type of QC. Please refer to the current LIMS control limits for the windows.

14.28.1 If the LCS does not fall within established control limits, the macro will ask the user to place another vial of the LCS in autosampler position C3. Press <Enter> to continue.

14.28.2 If the LCS still does not meet the criteria, then the macro will ask the user to prepare another LCS and to place the vial for the new LCS in autosampler position C3. Press any key to continue.

14.28.3 If the LCS still does not work, the macro will essentially begin again at Step 14.28.1. Please note that there is a possibility of an infinite loop occurring at this step. If the LCS does not work after 2 times through the decision tree, stop the macro and contact the metals lab supervisor for assistance.

14.29 The autosampler will now analyze 22 sample vials. If there are less than 22 vials left on the tray, then the autosampler will only analyze those samples. If the user needs to pause at any time during the analysis, press <F8>. The autosampler will stop after the current sample and wait until the <F8> key is pressed again. If the user presses the <F10> key, then the macro will stop immediately. The only way to resume a stopped analysis is to go to step 14.16 and restart the MERCURY macro.

14.30 When the autosampler has completed the analysis of the samples, the instrument will automatically analyze the CCB. The CCB should read back within ± 0.1 µg/L. If at any point in the decision tree below the CCB is within the limits, the macro will jump to step 14.31.

14.30.1 If the CCB does not meet the criteria, the macro will ask the user to place a new vial of the blank in autosampler position C1. Press any key to continue.

14.30.2 The instrument will then analyze the CCB again. If the CCB still does not meet the criteria, then the macro will autozero the instrument and rerun the CCB.

Rev 3/2/99 If autozero required, analytical sequence must be re-started, including standards, QC samples re-run from last acceptable CCB.

14.30.3 If the CCB does not read back within limits, the macro will essentially jump back to step 14.30.1. Please note that there is a possibility of an infinite loop occurring at this step. If the ICB refuses to work after 2 times through the decision tree, stop the macro and contact the metals lab supervisor for assistance.

14.31 When the CCB reads back within limits, the CCV will automatically be analyzed. The CCV is the midpoint calibration standard analyzed as a sample with the concentration

being read from the analytical curve. The percent recovery for the CCV must be within the control limits of 80%-120% of the true value. If the CCV recovers within the control windows before the macro reslopes, then the macro will jump to Step 14.32.

14.31.1 If the CCV fails to recover within the control limits, the macro will ask the analyst to place a new vial of the CCV in autosampler position C2. When this is complete, press any key to continue the analysis.

re-sloping no longer an option [illegible] 8/2/99

~~14.31.2 If the CCV fails again, the macro will try to reslope the calibration based on an analysis of the midpoint standard. If the reslope fails, then the macro will rerun the standards, set the autosampler to rerun all samples since the last good ICV or CCV, and start again at Step 14.26.~~

~~14.31.3 If the reslope has a correlation coefficient greater than 0.995, then the macro will set the autosampler to rerun all samples since the last good ICV or CCV and start again at Step 14.26.~~

14.32 If the CCV recovers within control limits, then start again at Step 14.29 with the next set of samples to be analyzed. If there are no more samples to analyze, then go to Step 14.33.

14.33 Check over the raw data to make sure that all of the samples are within the calibration range of the instrument. If any samples are above the calibration range of the curve, mark the sample number and appropriate dilution factor on the ID/WT sheet to be analyzed with the other dilutions at the end of the run. Dilutions may be made on the sample only if the diluent used has the correct amount of reagents in it. Do not use ASTM Type II water for dilutions. Make up a Blank solution of reagent water and reagents to use as the diluent.

15.0 FLOW CHART

Not Applicable

16.0 CALCULATIONS/DATA HANDLING

16.1 The concentration of each sample is read directly from the computer printout. Dilution factors should be taken into account in the ID/WT file.

16.1.1 Assuming that the instrument did not correct a concentration due to analyst error, the following calculation would be used:

$C_{Final} = C_{Instr} * DF_{Digest} * DF_{Subseq}$,, where

C_{Final} is the final reported concentration of the analyte
C_{Instr} is the concentration as read from the instrument data printout
DF_{Digest} is the digestion dilution factor
DF_{Subseq} is any dilution done subsequent to the digestion dilution

16.2 All samples should be reported to the correct number of significant figures. The significant figure truncation should not be performed until all data calculation have taken place.

16.2.1 Solid samples must be reported in mg/kg.

16.2.1.1 For sample concentrations <100 mg/kg, report 2 significant figures.

16.2.1.1 For sample concentrations ≥100 mg/kg, report 3 significant figures.

16.2.1.1 For QC, always report one additional significant figure.

16.2.2 Aqueous samples must be reported in ug/L.

16.2.2.1 For sample concentrations <1 ppb, report 1 significant figure.

16.2.2.2 For sample concentrations ≥1 ppb and <100 ppb, report 2 significant figures.

16.2.2.3 For sample concentrations ≥100 ppb, report 3 significant figures.

16.2.2.4 For QC, always report one additional significant figure.

16.2.3 Extracted samples for all metals must be reported in mg/L.

16.2.3.1 For sample concentrations <0.001 mg/L, report 1 significant figure.

16.2.3.2 For sample concentrations ≥0.001 mg/L and <0.100 mg/L, report 2 significant figures.

16.2.3.3 For sample concentrations ≥0.100 mg/L, report 3 significant figures.

16.2.3.4 For QC, always report one additional significant figure.

17.0 DATA REPORTING

See appendices F, H, I, and J for data reporting.

18.0 QUALITY ASSURANCE

18.1 All quality control data should be maintained and available for easy reference or inspection.

18.2 A calibration curve must be prepared each day with a minimum of a reagent blank and three standards. The correlation coefficient must be ≥ 0.995. If this fails the problem must be corrected.

18.3 IDL and MDL studies must be performed on an annual basis.

18.3.1 To calculate an IDL, analyze ten cups of Blank solution in series. Calculate the standard deviation of a small population, and multiply this result by three. There is also a spreadsheet located on the computer network that will perform this calculation for you. Please see the metals lab supervisor if you need assistance in using this program.

18.3.2 To calculate an MDL, analyze ten cups of a low concentration standard, typically at a concentration at or near the detection limit. Calculate the standard deviation of a small population and multiply the result by the Student's T value for (n-1) degrees of freedom. If the concentration of the standard ran is greater than ten times the calculated MDL, and the concentration of the standard ran is above the detection limit reported to clients, the MDL must be performed at lower concentration. If the standard concentration is less than ten times the calculated MDL or if the standard used for the analysis was at or below the lowest reporting limit on LIMS, the MDL is acceptable. There is also a spreadsheet located on the computer network that will perform this calculation for you. Please see the metals lab supervisor if you need assistance in using this program.

18.4 Dilute and reanalyze all samples that have concentrations greater than the highest standard of the analytical curve.

18.5 Include a minimum of one laboratory blank per sample digestion batch to determine if contamination or any memory effects are occurring. This laboratory blank must be carried through the sample preparation procedure.

18.6 Analyze one spike and one matrix spike duplicate (MSD) at a frequency of at least 1 in 20. A spike and matrix spike duplicate are samples into which a calculated extra amount of metal is pipetted in. The spike measures the accuracy of the sample preparation method and the MSD checks the precision of the method.

18.7 **Standard addition**: The Method of Standard Additions (MSA) shall be used for all EP extracts. MSAs must also be performed on all TCLP extracts that have spike recoveries less than 50%. The standard-addition technique involves adding known amounts of standard to one or more aliquots of the process sample solution. This technique compensates for a sample constitute that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct additive interferences which cause a baseline shift. The simple version of this technique is the single addition method, in which identical aliquots of the sample solution, each of

volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_X is calculated:

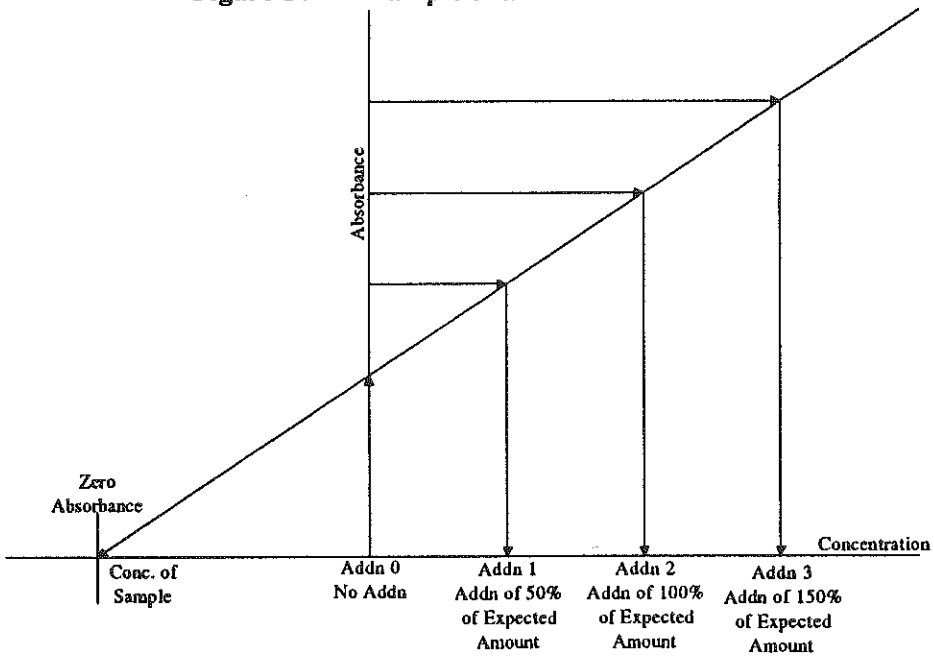
$$C_X = \frac{S_B * V_S * C_S}{(S_A - S_B) * V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear and the correlation coefficient must be ≥ 0.995.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

Figure 1 An Example of an MSA curve



18.8 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

NOTE: Steps 18.8.2 through 18.8.6 must be performed every time the instrument is calibrated.

18.8.1 Calibrate the instrument using at least three standards and a blank.

18.8.2 An ICB (Initial Calibration Blank) is analyzed after the calibration. The results of this blank are to be within ± 0.1 µg/L. If the blank is not within ± 0.1 µg/L, correct the problem, and restart the analysis from the beginning.

18.8.3 An ICV (Initial Calibration Verification) is placed after the ICB. Percent recovery limits are 90% to 110% of the concentration. If the percent recovery for

this standard is not within the acceptance limits, correct the problem, recalibrate if necessary, and restart the analysis.

18.8.4 An LCS (Laboratory Check Standard), which must come from a different primary source than the calibration standards, is placed after the ICV in each run. Percent recovery limits are 80% to 120% of the concentration unless control limits have been established. If the percent recovery for this standard is not within the acceptance limits, correct the problem. If the instrument had to be recalibrated, restart the analysis from the beginning.

18.8.5 Verify the calibration after every 10 samples.

18.8.5.1 A CCV (Continuing Calibration Verification) is analyzed after every 10 samples, or sooner. Percent recovery limits are 80% to 120% of the concentration. If the percent recovery for this standard is not within the acceptance limits, correct the problem. When the problem has been corrected, analyze a CCV. If the CCV is within control limits, restart the analysis from the last good ICV or CCV. If the CCV is not within the control limits, repeat steps 18.8.1 through 18.8.4, and then reanalyze all samples since the last good ICV or CCV.

18.8.5.2 A CCB (Continuing Calibration Blank) is analyzed after the CCV. The results of this blank are to be within ± 0.1 µg/L. If the blank is not within ± 0.1 µg/L, correct the problem, and restart the analysis from the last good CCB or ICB.

18.8.6 At the end of each run, verify the calibration.

18.8.6.1 A CCV (Continuing Calibration Verification) is analyzed after every 10 samples, or sooner. Percent recovery limits are 80% to 120% of the concentration. If the percent recovery for this standard is not within the acceptance limits, correct the problem. When the problem has been corrected, analyze a CCV. If the CCV is within control limits, restart the analysis from the last good ICV or CCV. If the CCV is not within the

control limits, repeat steps 18.8.1 through 18.8.4, and then reanalyze all samples since the last good ICV or CCV.

18.8.6.2 A CCB (Continuing Calibration Blank) is analyzed after the CCV. The results of this blank are to be within ± 0.1 µg/L. If the blank is not within ± 0.1 µg/L, correct the problem, and restart the analysis from the last good CCB or ICB.

18.9 A new analytical curve must be ran every 24 hours.

18.10 If the % RSD of the replicates for a sample is greater than 20% and the concentration of the sample is greater than the reporting limit, reanalyze the sample once. If the % RSD is again greater than 20% on a sample, qualify the data with data Qualifier number 10.

19.0 ANALYST CERTIFICATION

See Appendix E

20.0 REFERENCES

20.1 U.S. Environmental Protection Agency. Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique) Method 7471A, SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, Revision 0, September 1994.

20.2 U.S. Environmental Protection Agency. Determination of Mercury in Sediments by Cold Vapor Atomic Absorption Spectrometry Method 245.5, revision 2.3, EPA-600/4-91/010, June 1991.

20.3 U.S. Environmental Protection Agency. Mercury (Automated Cold Vapor Technique) Method 245.2 1974, EPA-600/4-79-020, revised March 1983.

20.4 Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

20.5 Leeman Labs PS Series ICP/Eschelle Spectrometers Reference Manual Rev. 1.0, May 1990.

21.0 APPENDICES

See attached pages.

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

CYANIDE, TOTAL

LACHAT AUTOANALYZER

USEPA METHOD 335.4/9012A (MODIFIED)

CONTROLLED DOCUMENT DO NOT COPY
TriMatrix Laboratories, Inc.

APPROVALS:

Inorganic Manager: _____ Date: 8/11/99
Douglas E. Kriscunas

QA Manager: _____ Date: 8/11/99
Rick D. Wilburn

Laboratory Manager: _____ Date: 8/11/99
Douglas E. Kriscunas

Procedure Number: GR-02-100
Revision Number: 2.1

Date Initiated: 7/23/93
Effective Date: 8/1/99

Date Revised: 8/11/99
Pages Revised: 3, 10, 11

By: Jodi L. Blouw

Total Number of Pages: 20

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of cyanide in drinking and surface waters, domestic and industrial wastes, soil and sludge.

1.2 The applicable range is 0.005 to 0.50 mg/L.

1.3 For water and wastewater the routine reporting limit for this method is 0.05 mg/L. The minimum reporting limit is 0.005 mg/L.

1.4 For soils and sludge the routine reporting limit for this method is 0.5 mg/kg (dry). The minimum reporting limit is 0.05 mg/kg (dry). For waste, the limits are the same as soil and sludge above but on an "as received" basis.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Methods for the Determination of Inorganic Substances in Environmental Samples,* August, 1993, "Determination of Total Cyanide by Semi-Automated Colorimetry", Method 335.4, Revision 1.0, August, 1993.

2.2 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, December, 1996, Method 9012A, "Total and Amenable Cyanide (Automated Colorimetric, with Off-Line Distillation)".

3.0 SUMMARY OF PROCEDURE

3.1 Total and/or amenable cyanide from alkaline distillates is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH lower than 8. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The color is read at 570 nm.

4.0 PARAMETER OR COMPOUND LIST

4.1 Cyanide, Total

4.2 Cyanide, Amenable

5.0 REFERENCED SOPs

5.1 TriMatrix SOP number GR-18-106, *Cyanide, Total, Preliminary Macro-Distillation*, most current version.

5.2 TriMatrix SOP number GR-18-109, *Cyanide, Preliminary Midi-Distillation*, most current version.

5.3 TriMatrix SOP number GR-18-105, *Cyanide, Amenable to Chlorination, Preliminary Distillation*, most current version.

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5.4 TriMatrix SOP number GR-02-103, *Lachat Quik Chem AE Operation*, most current version.

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Distillation will remove most substances that cause interference. See TriMatrix SOP numbers GR-18-106, GR-18-109, and GR-18-105 for the preliminary distillation procedure. For analytical corrective action procedures, see TriMatrix SOP number GR-10-106, *Inorganic Laboratory Corrective Actions*.

7.0 SAFETY PRECAUTIONS

7.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the TriMatrix Laboratories, Inc. Laboratory Safety Manual.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Waters and wastewaters are to be collected in opaque brown, inert plastic bottles and preserved with sodium hydroxide to a pH of 12 to 12.5.

8.2 Wastes, sludges, and soils are to be collected in inert bottles with no preservative added.

8.3 All samples should be stored at 4°C until time of analysis.

8.4 Waters and wastewaters must be homogenized by shaking just prior to removing a sample aliquot. Wastes, sludges, and soils must be homogenized using an appropriate mixing procedure prior to analysis.

8.5 Analysis must be performed within 14 days of sample collection.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Lachat QuickChem Automated Flow Injection Analyzer which includes:

- Automatic sampler
- Proportioning pump
- Injection valve module with a 150 cm 0.8 mm i.d. sample loop
- Flow Cell, 10 mm, 80 uL
- Interference Filter Wavelength, 570 nm
- Heater module
- Reaction module 10-204-00-1-A

9.2 Degassing wand

9.3 Standard vials

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9.4 Sample tubes

9.5 10 mL Buret

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Maintenance activities are covered in the Lachat Autoanalyzer SOP, TriMatrix SOP number GR-02-103.

11.0 CHEMICALS AND REAGENTS

11.1 Reagent Water. ASTM Type II, Milli-Q.

11.2 Indicator Solution: Dissolve 0.020 g p-dimethylaminobenzal-rhodanine in 100 mL acetone.

11.3 Potassium chromate (5% w/v) indicator solution, K_2CrO_4

11.3.1 purchased from BANCO.

11.4 Standard Sodium Chloride

11.4.1 Dissolve 1.125 g NaCl (dried at 140°C) in reagent water and dilute to 1000 mL.

11.5 Standard silver nitrate titrant: Dissolve 3.27 g $AgNO_3$ in 1 L reagent water. Standardize against standard NaCl solution, using the argentometric method with K_2CrO_4 indicator.

11.5.1 $AgNO_3$ Standardization Procedure: Place 10.0 mL of the NaCl standard and ~100 mL of reagent water into a beaker. Add 1 mL of K_2CrO_4 indicator solution. Titrate with the $AgNO_3$ until a pinkish yellow end point is attained.

11.5.2 Correction factor calculation:

$$\frac{A}{B} = C$$

where:

A = mL of NaCl standard titrated
B = mL of $AgNO_3$ titrant used
C = correction factor

11.6 0.25M Sodium Hydroxide: In a 1 L volumetric flask dissolve 10.0 g of sodium hydroxide pellets in 800 mL reagent water. Dilute to 1000 mL with reagent water. Invert several times to mix. May be stored in an inert plastic bottle at room temperature for up to 6 months.

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11.7 Phosphate Buffer, 0.71M by Volume: In a 1 L volumetric flask, dissolve 97 g anhydrous potassium dihydrogen phosphate (potassium phosphate, monobasic, anhydrous, KH_2PO_4) in approximately 800 mL of reagent water. Dilute to the mark with reagent water and invert several times until well mixed. May be stored in an inert plastic bottle at room temperature for up to 6 months.

11.8 Chloramine-T: In a 500 mL volumetric flask, dissolve 2.0 g chloramine-T hydrate in 400 mL reagent water. Dilute to mark with reagent water and invert several times to mix. May be stored in an inert plastic bottle at 4°C for up to 1 week.

11.9 Pyridine-Barbituric Acid Reagent by Volume: In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 mL reagent water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) with stirring and mix until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid (12M HCl) and mix. Transfer to a 1 L volumetric flask, dilute to the mark with reagent water, and invert. May be stored in an inert plastic bottle at 4°C for up to 6 months.

12.0 STANDARDS PREPARATION

12.1 Primary Stock Standard

12.1.1 Dissolve 1.255 g of potassium cyanide and 1.0 g of potassium hydroxide in 400 mL of reagent water in a 500 mL volumetric flask. Dilute to volume with reagent water. Concentration is 1000 mg/L. **Caution: KCN is highly toxic. Avoid inhalation of dust or contact with the solid or solutions.** This standard may be kept for as long as six months.

Note: The primary stock standard must be titrated each time it is used to prepare secondary, tertiary, or working standards. See titration procedure (section 12.2).

12.2 Primary stock standard titration procedure:

12.2.1 Dilute 5 mL of the 1000 mg/L stock standard to 100 mL using 0.25N sodium hydroxide solution.

12.2.2 Add 0.5 mL of indicator solution.

12.2.3 Titrate with standard $AgNO_3$ titrant until the first change in color occurs from a canary yellow to a salmon hue.

12.2.4 Titrate a NaOH dilution water blank.

12.2.5 Cyanide Concentration Calculation

$$\text{mg } CN^- / L = \frac{(A - B) \times 1000 \times C}{\text{ml of original sample}}$$

where:

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A = mL of titrant for the standard
B = mL of titrant for the blank
C = correction factor from section 11.5.2

12.3 Secondary Stock Standard

12.3.1 The secondary standard is prepared by adding 10 mL of the primary stock standard to ~60 mL 0.25N NaOH in a 100 mL volumetric flask. Dilute to volume with 0.25N NaOH. Concentration is 100 mg/L. Prepare this standard every two weeks.

12.4 Tertiary Stock Standard

12.4.1 The tertiary standard is prepared by adding 10 mL of the secondary standard to 60 mL of 0.25N NaOH in a 100 mL volumetric flask. Dilute to volume with 0.25N NaOH. Concentration is 10 mg/L. Prepare this standard every two weeks.

12.5 Quarternary Stock Standard

12.5.1 The quarternary stock standard is prepared by adding 10 mL of the tertiary standard to 60 mL of 0.25N NaOH in a 100 mL volumetric flask. Dilute to volume with 0.25N NaOH. Concentration is 1 mg/L. Prepare this standard every 2 weeks.

12.6 Working Standards

Concentration mg/L	mL of standard in NaOH
0.5	5 mL of 10 ppm/100 mL 0.25N NaOH
0.2	20 mL of 1 ppm/100 mL 0.25N NaOH
0.1	20 mL of 1 ppm/200 mL 0.25N NaOH
0.05	10 mL of 0.5 ppm/100 mL 0.25N NaOH
0.02	10 mL of 0.2 ppm/100 mL 0.25N NaOH
0.005	10 mL of 0.1 ppm/200 mL 0.25N NaOH

12.6.1 Working standards are prepared every two weeks.

12.6.2 If sulfide interferences have been detected during the pre-treatment of the samples, the samples have been treated with bismuth nitrate. A separate curve must be prepared and analyzed, using working standards that have also been treated with bismuth nitrate. To the volumes specified above, pipet out 10 mL of the 0.25N NaOH solution, and replace it with 10 mL of bismuth nitrate solution prior to the addition of the cyanide solution.

12.7 Separate stock standard preparation for quality control use.

12.7.1 Prepare a second primary stock standard (1000 mg/L) from a separate discrete stock KCN chemical. See section 12.1. Titrate as in section 12.2.

12.7.2 Prepare a 100 mg/L secondary standard from the separate discrete 1000 mg/L primary stock standard.

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12.7.3 Prepare a 5.0 mg/L tertiary standard from the 100 mg/L separate discrete stock standard.

12.7.4 Prepare a 0.05 mg/L working standard from the separate discrete 5.0 mg/L stock standard (see preparation below).

12.7.4.1 Standard Preparation:

mL of stock standard into mL of 0.25N NaOH	Concentration
10 mL of the 1000 mg/L into 100 mL	100 mg/L
5 mL of the 100 mg/L into 100 mL	5 mg/L
1.0 mL of the 5.0 mg/L into 100 mL	0.05 mg/L

12.8 All stock standards must be labeled with the following information:

- expiration date
- initials of preparer
- date of preparation
- concentration
- name of parameter
- standard log number as it appears in the standard logbook
- amounts of each compound contained and diluted volume

12.9 Working standards must be labeled with the following information:

- initials of the preparer
- date of preparation
- concentration
- name of the parameter
- expiration date
- stock standard number

12.10 All standard preparation must be recorded in the appropriate standard logbook with its unique ID number. See attachments 21.1 and 21.2 for standard logbook page examples.

13.0 SAMPLE PREPARATION

13.1 See TriMatrix SOP numbers GR-18-106 and GR-18-109 for sample pre-treatment distillation.

13.2 See TriMatrix SOP number GR-18-105 for amenable sample pre-treatment distillation.

14.0 CALIBRATION PROCEDURES

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14.1 The calibration curve for the analysis is prepared using the 0.5 mg/L, 0.2 mg/L, 0.10 mg/L, 0.05 mg/L, 0.02 mg/L, and 0.005 mg/L working standards prepared in section 12.6. See section 15.0 for the calibration procedure.

15.0 ANALYTICAL PROCEDURE

(Please refer to the Lachat Autoanalyzer general SOP (GR-02-103) for more detailed instructions for running this instrument).

15.1 Prepare channel 3 for cyanide analysis by connecting the cyanide manifold to the valve and detector.

15.2 Inspect modules on the Lachat autoanalyzer for proper connections.

15.3 Turn on power to all modules. Allow heater to warm up to 60°C. This takes approximately 30 minutes.

15.4 Degas all reagents including reagent water used for rinse.

15.5 Place reagent transmission lines into proper containers. Place the line labeled "rinse" into the degassed reagent water. Raise tension levers on pump tube cassettes.

15.6 Select desired method. Pump system until a stable baseline is attained.

15.7 Place calibration standards and blank in sample tray in descending order of concentration.

15.8 Initiate calibration. Be sure printer is on to record standard peaks.

15.9 When calibration is complete, review standard curve and calibration report. If acceptable, approve calibration.

15.10 Place samples in sample tubes. Arrange sample tubes in sample tray in desired order. Type in run data and save under chosen name.

15.11 Submit sample tray. Be sure printer is on to record sample peaks.

15.12 At end of run, place all transmission lines in water, flush system and pump dry.

15.13 Turn off pump, all modules, and release pump tube cassettes.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The instrument regresses all sample data against the calibration curves, and prints out concentration. See attachment 21.3 for Lachat calibration and run data examples.

16.2 Basic rules apply for significant figure reporting: report 3 figures over 100 mg/L, report 2 figures below 100 mg/L, and report only 1 figure below 0.010 mg/L.

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17.0 DATA REPORTING AND DELIVERABLES

17.1 The following must be attached to the laboratory benchsheet for each batch turned in:

- calibration statistics report
- peak printouts for calibration and samples
- calibration curve printout
- runtime report
- calibration report
- pretreatment sheets

17.2 The instrument logbook must be filled out for each batch turned in with the following information:

- date analyzed
- analysts initials
- method name and number
- calibration standards used
- client name and sample numbers analyzed

17.2.1 See attachment 21.4 for an example instrument logbook page.

17.3 The following data is to be put on the benchsheet for each batch turned in:

- ICV, ICB, LCS, MPB, reported conc., CCV, CCB, SPK, MSD or DUP, LFB
- Instrument number, owner, date run, supervisor, stock standard number, wavelength, cell path
- Standard values, observed standard values, working standard number's

17.4 See attachments 21.5, 21.6, and 21.7 for copies of total and amenable cyanide benchsheets, and a total cyanide batch detail report.

18.0 QUALITY ASSURANCE

18.1 Method and matrix QC must be analyzed with each batch.

18.1.1 Method QC consists of a Laboratory Control Sample (LCS), Instrument Blank (BLK), Method Preparation Blank (MPB), a high and a low level Laboratory Fortified Blank (LFB), Initial Calibration Verification (ICV), Initial Calibration Blank (ICB), Continuing Calibration Verifications (CCV), Continuing Calibration Blanks (CCB) and a Detection Limit Confirmation Standard (CRL). Method and matrix QC must be distilled for each batch. A batch consists of a maximum of 20 samples per matrix, and may be left open for 2 weeks.

18.1.1.1 The LFB and MPB are pretreated QC. See TriMatrix SOP numbers GR-18-106, GR-18-109, and GR-18-105 for the preparation and distillation of the LFB and MPB. The acceptance limits for the LFB are on the benchsheet. The MPB result must be less than the reporting limit for the analysis. A low level LFB, a high level

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LFB, and a MPB are distilled every time a new batch is opened. A MPB and a low or a high LFB are additionally distilled every day samples are distilled for that batch.

18.1.1.2 The LCS is a non-distilled separate discrete working standard analyzed with each run to validate the standard curve for the run. The separate discrete 0.05 mg/L standard (prepared in section 12.7.4) is analyzed as the LCS. The accuracy limits for the LSC percent recovery are on the benchsheet.

18.1.1.3 The BLK is an aliquot of 0.25N NaOH analyzed like a sample. The results must be less that the reporting limit for the analysis.

18.1.1.4 The ICV is an aliquot of a midrange standard analyzed immediately after the curve. The acceptance limits for the ICV are 90-110 percent of the true value.

18.1.1.5 The ICB is an aliquot of non-distilled 0.25N NaOH analyzed immediately after the ICV. The result must be less than the reporting limit for the analysis.

18.1.1.6 The CCVs are aliquots of midrange standards analyzed after every ten samples and at the end of every batch. The accuracy range for the CCVs are 90-110 percent of the true value. (Included in the ten samples are the LCS, BLK, SPK1, and DUP.)

18.1.1.7 The CCBs are aliquots of 0.25N NaOH analyzed after every ten samples (after the CCVs) and at the end of each batch. The results must be less than the reporting limits for the analysis.

18.1.1.8 The CRDL is a non-distilled aliquot of the 0.005 mg/L standard used for the curve analyzed as a sample. The recovery limits are 0.002 – 0.008 mg/L.

18.1.2 Matrix QC consists of two matrix spikes (SPK1 and SPK2) and a calculated Matrix Spike Duplicate (MSD) or a duplicate (DUP). Matrix spikes are performed at a frequency of 1 set per 20 samples per matrix.

18.1.2.1 The SPK1 and SPK2 are sample aliquots spiked with a known amount of analyte, distilled and analyzed like a sample. See TriMatrix SOP numbers GR-18-106, GR-18-109, and GR-18-105 for the preparation and distillation of the spikes. The accuracy limits for SPK1 and SPK2 are printed on the benchsheet.

18.1.2.2 The MSD is the percent difference between the SPK1 and SPK2 detected concentrations. The MSD precision limit is printed on the benchsheet.

18.1.2.3 The DUP is analyzed for amenable cyanide only (see TriMatrix SOP number GR-18-105). A DUP is a second aliquot of sample re-analyzed. The precision limit for the DUP is printed on the benchsheet.

18.2 Method Detection Limit Studies

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18.2.1 A Method Detection Limit (MDL) study must be performed using this method. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. Actual reporting limits are derived from the MDL study. The minimum possible reporting limit is equal to the amount spiked in the MDL study, provided the MDL passed. The reporting limit actually achieved in any given analysis will vary depending on instrument sensitivity, matrix effects, and dilutions. When applicable, an MDL study must be analyzed for both waters and soils.

18.2.2 The procedure followed for a MDL study is based on the method given in the Federal Register, Part 136, Appendix B, latest revision.

18.2.3 The concentration of the standard used as the low point in the initial calibration curve must equal the spiked level of the MDL study. During actual sample analysis, when reporting to the minimum reporting limit, this same standard concentration must again be the low point of the calibration curve.

18.2.4 Seven replicate analyses are performed using reagent water or clean sand spiked with the analyte(s) of interest at the estimated minimum detectable concentration. Four of the water replicates can also be used for analyst certification/method validation, as described in section 19.0.

18.2.5 If a blank measurement is required to calculate the measured level of an analyte, seven separate blanks must be analyzed, one after each of the seven MDL samples. The average blank measurement is subtracted from all seven MDL analyses.

18.2.6 The standard deviation of the amount found (blank-subtracted if necessary) for the analyte(s) using all seven analyses is calculated and multiplied by 3.143. The resulting number is the calculated MDL.

18.2.7 If the amount spiked is between the calculated MDL and ≤ 5 times the calculated MDL, and there are no zero percent recoveries in the set of seven, the MDL is acceptable. If not, the MDL must be re-analyzed, only for the analyte(s) that did not pass. If the study needs to be re-analyzed at a different concentration, the entire set of seven needs to be re-analyzed. If the study does not pass due to poor reproducibility on one of the samples, only that one analysis needs to be re-analyzed. All seven analyses do not need to be analyzed in the same analytical batch.

18.2.8 If at any time the MDL level is above a client's or state's desired reporting limit, the calculated MDL value may be used for a reporting limit, provided the result is narrated. The narration must state that the reporting limit is based on the calculated MDL value, and that the analyte(s), when spiked at that level, was not observed.

19.0 ANALYST CERTIFICATION/METHOD VALIDATION

19.1 Before the analysis of any actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running a one time analyst certification. While the analyst certification is not instrument dependent, this certification is required on every instrument that will be running samples to demonstrate instrument ability to generate acceptable accuracy and precision.

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19.2 Prepare a LCS at a level that will give a concentration of approximately 0.05 mg/L.

19.3 Analyze the LCS four times following the SOP.

19.4 Calculate the average percent recovery, and the standard deviation of the percent recoveries, using the four results.

19.5 Each recovery must be in the range 70-130 percent and the standard deviation must be less than or equal to 20. If both these criteria are met, the analyst certification is acceptable. The analyst and the system are now authorized to run samples by this method.

19.5 If either criteria are not met, locate and correct the source of the problem and repeat the test. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds beginning with section 19.2. Samples may not be analyzed by any analyst or on any instrument until the analyst certification has been successfully completed. Copies of the successful analyst certifications/method validations spreadsheet and raw data should be given to the Quality Assurance Manager.

20.0 REFERENCES

20.1 *Methods for the Determination of Inorganic Substances in Environmental Samples,* August, 1993, "Determination of Total Cyanide by Semi-Automated Colorimetry", Method 335.4, Revision 1.0, August, 1993.

20.2 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, December, 1996, Method 9012A, "Total and Amenable Cyanide (Automated Colorimetric, with Off-Line Distillation)".

20.3 *Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995,* 4500-CN⁻ Cyanide, E. Colorimetric Method.

20.4 Methods Manual for the QuickChem Automated Ion Analyzer, Lachat Instruments.

21.0 ATTACHMENTS/APPENDICES

21.1 Stock Standard Record Book Example

21.2 Working Standard Record Book Example

21.3 Lachat Calibration Example

21.4 Instrument Logbook Example

21.5 Benchsheet, Amenable Cyanide

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21.6 Benchsheet, Total Cyanide

21.7 Total Cyanide Batch Detail Report

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Attachment 21.1
Stock Standard Record Book Example

Standard Record Book - Stock Standards

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Date	Preparer	Parameter(s)	Concentration	Preparation Procedure	Solvent	Preservative	Standard Reference Number	Shelf Life
12/30/98	JLB	Phenol	100 ppm	10ml 1000ppm / 100ml	H_2O	–	321D.18.4	
12/30/98	JLB	Phenol	10 ppm	10ml 100ppm / 100ml	H_2O	–	321D.18.4.1	
12/30/98	JLB	Phenol	100 ppm	10ml 1000ppm / 100ml	H_2O	–	321E.12.4	
1/4/99	JLB	CN⁻	100 ppm	10ml 1000ppm / 100ml	0.25N NaOH	–	152D.1.4	
↓	↓	↓	10	10ml 100ppm / 100ml	↓	–	152D.1.4.1	
JLB	JLB	JLB	1	10ml 10ppm / 100ml	JLB	–	152D.1.4.1.1	
↓	↓	↓	100 LCS	10ml 1000ppm / 100ml	↓	–	152B.20.4	
1/4/99	JLB	CN⁻	5 ppm LCS	5ml 100ppm / 100ml	0.25N NaOH	–	152B.20.4.1	
1/5/99	JLB	Phenol	100ppm	10ml 1000ppm / 100ml	H_2O	–	321D.18.5	
↓	↓	↓	10 ppm	10ml 100ppm / 100ml	H_2O	–	321D.18.5.1	
1/5/99	JLB	Phenol	100ppm LCS	10ml 1000ppm / 100ml	H_2O	–	321E.12.5	
1/11/99	NLB	SO_4	1000 ppm	0.7395g Na_2SO_4 / 500mls	H_2O	–	225B.43	
JLB ~~1/12/99~~ 12/31/98	JLB	Alkalinity	1190 mg/L	2.000g sodium bicarb. / 1L	H_2O	–	193E.16	
12/31/98	JLB	Alk., Carb.	1887 mg/L	2g Na_2CO_3 / 1L	H_2O	–	201B.4	
1/13/99	JLB	Phenol	100ppm	10ml 1000ppm / 100ml	H_2O	–	321D.18.6	
↓	↓	↓	10	10ml 100ppm / 100ml	H_2O	–	321D.18.6.1	
1/13/99	JLB	Phenol	100 ppm LCS	10ml 1000ppm / 100ml	H_2O	–	321E.12.6	
1/13/99	NLB	SO_4	100 ppm	5mls of 225B.43 / 50mls	H_2O	–	225B.43.1	

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Attachment 21.2
Working Standard Record Book Example

Standard Record Book - Working Standards

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Date	Preparer	Parameter(s)	Concentration	Preparation Procedure	Solvent	Preservative	Standard Reference Number	Shelf Life
1/4/99	JLB	CN-	0.02 ppm	10ml 0.2ppm / 100ml	0.25N NaOH	—	152D14.1.3.1	
1/4/99	JLB	CN-	0.005 ppm	10ml 0.1ppm / 100ml	↓	—	152D.1.4.1.1	.1.1
1/4/99	JLB	CN-	0.05 ppm CS	1ml 5ppm / 100ml	0.25N NaOH	—	152B.2.04	1.1
1/4/99	JMB	TPO4	25 ppm	25 ml of 100ppm / 100 ml	0.11M H_2SO_4	—	167V.1.1.39	
			10 ppm	10 ml of 100ppm / 100 ml		—	167V.1.1.40	
			5 ppm	5 ml of 100ppm / 100 ml		—	167V.1.1.	41
			2.0 ppm	2ml of 100ppm / 100 ml		—	167V.1.1.	42
			1.0 ppm	1ml of 100ppm / 100 ml		—	167V.1.1.	43
			0.5 ppm	1ml of 100ppm / 200 ml		—	167V.1.1.	44
			0.1 ppm	10ml of 1.0ppm / 100 ml		—	167V.1.1.	43.1
			0.05 ppm	10 ml of 0.5ppm / 100 ml		—	167V.1.1	44.1
1/4/99	JMB	TPO4	0.01 ppm	20ml of 0.1ppm / 200 ml	0.11M H_2SO_4	—	167V.1.1.	43.1.1
1/5/99	JLB	Phenol	2.0 ppm	20ml 10ppm / 100ml	H_2O	—	321D.18.5	.1.1
			0.5	5ml 10ppm / 100ml		—	321D.18.5.1.2	
			0.2	10ml 2.0ppm / 100ml		—	321D.18.5.1.	1.1
			0.05	10ml 0.5 ppm / 100ml		—	321D.18.5	1.2.1
			0.02	10ml 0.2 ppm / 100ml		—	321D.18.5.	1.1.1
			0.01	5ml 0.2ppm / 100ml		—	321D.18.5.	1.1.1.2
1/5/99	JLB	Phenol	0.20 ppm CS	200µl 10ppm / 100ml	H_2O	—	321F.12.5	1

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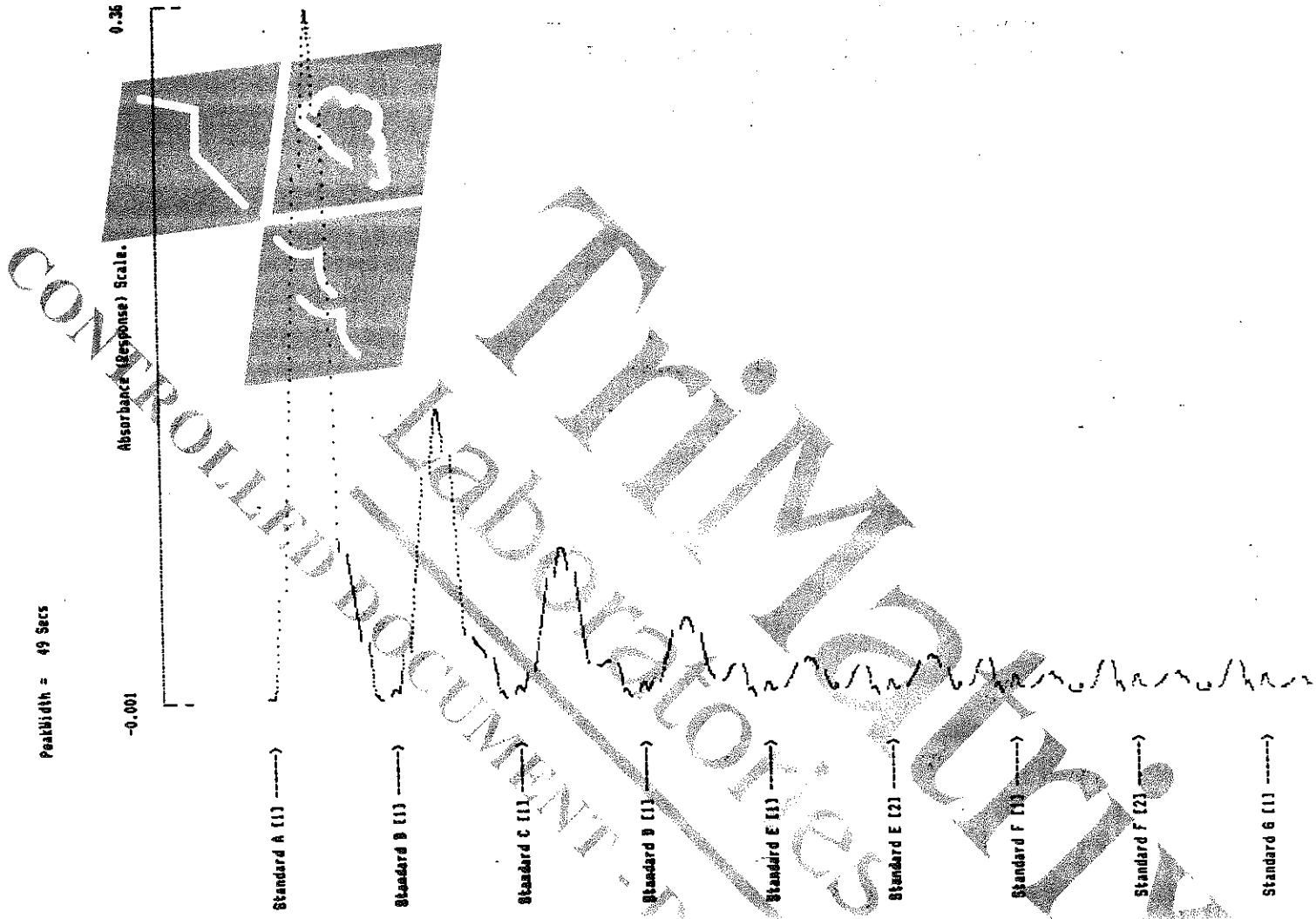
Attachment 21.3
Lachat Calibration Example



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Attachment 21.4
Instrument Logbook Example

Instrument Log Book Worksheet

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Date	Analyte	Method Reagent Reagent	Calibration Standards Used No. 1	No. 2	No. 3	No. 4	No. 5	Meets Calibration Requirements Yes	No	Sample Numbers	Changes or Repairs	Instrument Maintenance Log Page
1-5-99	CN	NaOH	2.4/1.0	0.5	0.1	0.05	0.01	—		Allied 214344-214346, 214348, 214349 Trout 214351 Ann Arbor 214261-214262 NP 214302-214303 Michigan 214164-214165		
1-5-99	NLB	NO3/NO2	1.0ppm	0.5	0.25	0.10	0.05	✓		Brochem 214342 Hemlock 214375 Trout Creek 214351-214352		
1-6-99	NLB	CN-	0.5	0.2	0.1	0.05	0.02/0.005	✓		Genesee 214210 Rotharm Michigan 214164 Sac ETDS		
1-6-99	JMB	PO4	1.0	0.5	0.1	0.05	0.01	✓		MIL PROV -214388 CRA-214401-214403 ETDS-214367 Hemlock-214374 Trout Creek-214351, 214352 Allenbach -214304		214404
#1 1-6-99	NLB	NO3/NO2	1.0ppm	0.5	0.25	0.10	0.05	✓		Kent CO (13) 214435-214447		
1-7-99	SAJ	TKN	10ppm	5.0ppm	2.0	1.0	0.5	✓		CRA 214401-403 Brochem 214343 MDL Study		
1-7-99	CN	NaOH	2.0/1.0	0.5	0.1	0.05	0.01	—		Kent 214435-214447 CRA 214401-214403 Trout 214352 Brochem 214343 Barrer 211226-211242, 211215-211224		
1-7-99	JMB	PO4	1.0ppm	0.5	0.1	0.05	0.01	✓		Allenbach-214304 MDL-Study		
#1 1-7-99	NLB	NO3/NO2	1.0ppm	0.5	0.25	0.10	0.05	✓		Kent CO 214462-214464, 214466		214474
1-8-99	SAJ	Cl-	150ppm/10ml	60/2ml	60/5ml	20	1.0	✓		Allied Waste - 214344-346, 214348-349 Kentco - 214435-474 Trout Creek - 214351-352 (MDL STUDY) City Well - 214353-372 Kent CO 214462-464		
#1 1-8-99	NLB	NO3/NO2	1.0ppm	0.50	0.25	0.10	0.05	✓		Kent CO 214559-214563 Welch 214481		
1-12-99	NLB	CN-	0.5ppm	0.2	0.1	0.05	0.02/0.005	✓		Barr 214577-584 Sterling 214397 MSI 214533 CRA 214466 Hemlock 214494 ETDS 214575-517 Allied 214459, 478 Lowell 214458 Sterling 214485-488 MDL CN midi total 3M 214264 Fed Mogul 214421		

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Approved By: 8/11/99 Area Manager

Attachment 21.5
Benchsheet, Amenable Cyanide

12-JAN-99 INORGANIC BENCHSHEET — AUTOMATED CHEMISTRY — WATER/WASTE WATER PAGE 1

Test#: 391. 1- 249.02
Parameter: CYANIDE,TOTAL
Method: CN/W-DIST/MU ODL: 0.05
Ref. Cit.: USEPA-335.4 Unit: mg/L
Batch: 138099 Sat 1 1/12/99

	STD VAL	OBS VAL	WKG STD NUMBER
1.	0.5	0.3992	152D.1.4.1.2
2.	0.2	0.1493	152D.1.4.1.3
3.	0.1	0.0763	152D.1.4.1.1.1
4.	0.05	0.0383	152D.1.4.1.2.1
5.	0.02	0.0157	152D.1.4.1.3.1
6.	0.005	0.0040	152D.1.4.1.1.1.1
7.			
8.			
9.			
10.			

Instrument #: 161
Benchsheet ID: 216780
Owner: JLB
Batch Opened Date: 1/12/99
Supervisor:
Est anal hrs: 10
Act anal hrs:
Samples in batch: 10
Stock std #:
Wavelength (nm):
Cell path (mm):

Comments:

Client Submittal Location	Sample	COC	QC	Anl.	Run Date	Wt/dil factor	Reported Conc.	ODL	QN	Spike Qty	% rec/dif	LCL-UCL	
ICV: Stk 152D.1.4.1.3							0.208	0.005		0.200	104	90-110	✓
ICB:							<0.005	0.005		XXXXXXXX XXXXXXXX		✓	
[redacted]													
29015- 454 Effluent T	214566		LV2				<0.05			✓			
[redacted]													
32451- 252 P1	214515		LV1				<0.05			✓			
[redacted]													
32451- 252	214516		LV1				<0.05			✓			
[redacted]													
32451- 252 P1	214517		LV1				<0.05			✓			
[redacted]													
32718- 648 SL #1 Grab	214397		LV2				<0.005	0.005		✓			
[redacted]													
32718- 649 SL #1 Grab	214485 *		LV2				<0.005	0.005		✓			
[redacted]													
32718- 649 SL #1 Grab	214487 *		LV2				<0.005	0.005		✓			
[redacted]													
32718- 649 SL #1 Grab	214488 *		LV2				<0.005	0.005		✓			
CCV: Stk 152D.1.4.1.3		Rep 1					0.211	0.005		0.20	106	90-110	✓
CCB:		Rep 1					<0.005	0.005		XXXXXXXX XXXXXXXX		✓	

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Attachment 21.6
Benchsheet, Total Cyanide

12-JAN-99 INORGANIC BENCHSHEET — AUTOMATED CHEMISTRY PAGE 1

Test#: [redacted]
Parameter: [redacted]
Method: [redacted]
Ref. Cit.: [redacted]
Batch: [redacted]

DDL: 0.005
Unit: mg/L

	STD VAL.	OBS VAL.	WAG STD NUMBER
1.			
2.			
3.			
4.			
5.			
6.			
7.			
8.			
9.			
10.			

Instrument #:
Benchsheet ID: 216778
Owner: JLP
Batch Opened Date: 1/12/99
Supervisor:
Est anal hrs: .25
Act anal hrs:
Samples in batch: 1
Stock std #:
Wavelength (nm):
Cell path (mm):

Comments:

Client Submittal Location	Sample	[redacted]	Wt/dil Factor	Dilution Factor	mg/l	% Sol.	Reported Conc.	DDL	QW	Spike Qty	% rec/dif
ICV: Stk											
ICB:										XXXXXXXX	
[redacted]										XXXXXXXX	
32891- 201 214421 Pond	LV1						<0.005	0.005	38	✓	
CCV: Stk 152D.1.4.1.3	Rep 3						0.206	0.005		0.20	103 ✓
CCB:	Rep 3						<0.005	0.005		XXXXXXXX	✓

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Attachment 21.7
Total Cyanide Batch Detail Report

15m7 J66t15m7 J66t

1999-JAN-12 15:09 BATCH DETAIL REPORT -- INORGANIC LABORATORY ANALYTICAL BATCH # 138099 PAGE 1 OF 3

Batch #	Opened	Owner	Seq	Complete	Control	Common name	Application	Ref cit	Qty samp	ICB	ICV	LCS	CCB	CCV
138099	12-JAN-99	JLB	2	NO	YES	CN/W-DIST/WTR	WATER	USEPA-335.4	23	1	1	1	6	6

	Seq	Sur-seq	QC bat	Run date	Anal	Sample	Appl	Det lim	Init conc	Final conc	Spike	Parameter	Type	%	LCL	UCL	QC	E	D	Ref cit
v	1.000	-		01/12/99	JLB		WATER	0.005		0.208	0.200	CYANIDE,TOTAL	ICV- 1	104	90	110				USEPA-335.4
v	2.000	-		01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	ICB- 1	0						USEPA-335.4
v	3.000	-	138066	01/12/99	JLB	214564	WW	0.05		<0.05		CYANIDE,TOTAL	REG-111							USEPA-335.4
v	4.000	-	137762	01/12/99	JLB	214515	WW	0.05		<0.05		CYANIDE,TOTAL	REG-108							USEPA-335.4
v	5.000	-	137762	01/12/99	JLB	214516	WW	0.05		<0.05		CYANIDE,TOTAL	REG-108							USEPA-335.4
v	6.000	-	138066	01/12/99	JLB	214517	WW	0.05		<0.05		CYANIDE,TOTAL	REG-111							USEPA-335.4
v	7.000	-	137762	01/12/99	JLB	214397	WW	0.005		<0.005		CYANIDE,TOTAL	REG-108							USEPA-335.4
v	8.000	-	137762	01/12/99	JLB	214485	WW	0.005		<0.005		CYANIDE,TOTAL	REG-108							USEPA-335.4
v	9.000	-	138066	01/12/99	JLB	214487	WW	0.005		<0.005		CYANIDE,TOTAL	REG-111							USEPA-335.4
v	10.000	-	138066	01/12/99	JLB	214488	WW	0.005		<0.005		CYANIDE,TOTAL	REG-111							USEPA-335.4
v	11.000	-		01/12/99	JLB		WATER	0.005		0.211	0.20	CYANIDE,TOTAL	CCV- 1	106	90	110				USEPA-335.4
v	12.000	-		01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	CCB- 1	0						USEPA-335.4
v	13.000	-	137762	01/12/99	JLB	214406	WW	0.005		<0.005		CYANIDE,TOTAL	REG-108							USEPA-335.4
v	14.000	-	137762	01/12/99	JLB	214454	WW	0.05		<0.05		CYANIDE,TOTAL	REG-108							USEPA-335.4
v	15.000	-		01/12/99	JLB		WATER	0.005		0.210	0.20	CYANIDE,TOTAL	CCV- 2	105	90	110				USEPA-335.4
v	16.000	-		01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	CCB- 2	0						USEPA-335.4
v	17.000	-		01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	BLK- 1	0						USEPA-335.4
v	18.000	-	17	01/12/99	JLB		WATER	0.005		0.052	0.05	CYANIDE,TOTAL	LCS- 1	104	90	110				USEPA-335.4
v	19.000	-	10 138066	01/12/99	JLB	214488	WW	0.005	<0.005	0.20	0.20	CYANIDE,TOTAL	MPK- 1	100	40	156				USEPA-335.4
v	20.000	-	19 138066	01/12/99	JLB	214488	WW	0.005	<0.005	0.19	0.20	CYANIDE,TOTAL	SPK- 2	95	40	156				USEPA-335.4
v	21.000	-	20 138066	01/12/99	JLB	214488	WW	0.005	0.20	0.19		CYANIDE,TOTAL	MSD- 1	5		20				USEPA-335.4
v	22.000	-	137762	01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	MPB-108	0						USEPA-335.4
v	23.000	-	22 137762	01/12/99	JLB		WATER	0.005		0.222	0.20	CYANIDE,TOTAL	LFB-108	111	77	129				USEPA-335.4
v	24.000	-		01/12/99	JLB		WATER	0.004		0.004	0.005	CYANIDE,TOTAL	CRL- 1	80	22	148				USEPA-335.4
v	25.000	-	137762	01/12/99	JLB	214459	WW	0.05		0.16		CYANIDE,TOTAL	REG-108							USEPA-9012 Mod.
v	26.000	-	137762	01/12/99	JLB	214458	WW	0.05		<0.05		CYANIDE,TOTAL	REG-108							USEPA-9012 Mod.
v	27.000	-		01/12/99	JLB		WATER	0.005		0.204	0.200	CYANIDE,TOTAL	CCV- 3	102	90	110				USEPA-335.4
v	28.000	-		01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	CCB- 5	0						USEPA-335.4
v	29.000	-	138066	01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	MPB-111	0						USEPA-335.4
v	30.000	-	29 138066	01/12/99	JLB		WATER	0.005		0.207	0.20	CYANIDE,TOTAL	LFB-111	104	77	129				USEPA-335.4
v	31.000	-	138066	01/12/99	JLB		WATER	0.005		<0.005		CYANIDE,TOTAL	MPB-211	0						USEPA-335.4
v	32.000	-	31 138066	01/12/99	JLB		WATER	0.005		0.018	0.02	CYANIDE,TOTAL	LFB-211	90	77	129				USEPA-335.4

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TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

VOLATILE ORGANIC COMPOUNDS BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

USEPA METHOD 8260B

USEPA METHOD 624

UNCONTROLLED DOCUMENT

APPROVALS:

Organics Manager: _____ Date: 5/28/98
Jeff P. Glaser

QA Manager: _____ Date: 5/28/98
Rick D. Wilburn

Laboratory Manager: _____ Date: 5/28/98
Douglas E. Kriscunas

Procedure Number: GR-04-104
Revision Number: 3.0

Date Initiated: 9/1/95
Effective Date: 7/1/97

Date Revised: 5/28/98
Pages Revised: All

By: Jeff Glaser

Total Number of Pages: 56

1.0 SCOPE AND APPLICATION

1.1 Method 8260B/624 is a gas chromatograph/mass spectrometry (GC/MS) procedure for determining volatile organic compounds in a variety of matrices. This method can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile water-soluble compounds generally have higher quantitation limits due to poor purging efficiencies. Such compounds include low molecuLar weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. It is applicable to nearly all type of samples, regardless of water content, including ground water, wastewater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The sample is introduced into the system using a purge and trap concentrator or by direct injection.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition*, Update III, Revision 2, December 1996, Method 8260B.

2.2 *Code of Federal Regulations, Title 40*, Part 136, Section 1, Appendix A, July 1, 1997, Methods 601 and 624.

3.0 SUMMARY OF PROCEDURE

3.1 When using the purge and trap technique, an inert gas is bubbled through the liquid sample at an ambient or slightly elevated temperature, and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and back flushed with inert gas to desorb the components onto a capillary column. The capillary column is temperature programmed to separate and elute the components, which are then detected with a mass spectrometer which provides qualitative or quantitative results.

3.2 Analytes are introduced into the mass spectrometer via a jet separator or a direct connection using an open-split interface. Identification of analytes is done by comparing their mass spectra with spectra of calibration standards. Quantitation is performed by comparing the response of the analytes quantitation ion (relative to its corresponding internal standard) with a five point calibration curve.

4.0 PARAMETER OR COMPOUND LIST

4.1 See Tables 1A and 1B.

5.0 REFERENCED SOPs

5.1 TriMatrix SOP number GR-04-105, *Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples*, most current version.

5.2 TriMatrix SOP number GR-3-124, *Volatile Laboratory Corrective Actions*, most current version.

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Whether purged or injected directly on column, interferences naturally present in the samples can cause elevated detection limits and interfere with the analysis. Naturally occurring interferences can vary considerably from site to site.

6.2 Sample contamination can also cause raised detection limits or false positives, and can come from a variety of sources. Improper sampling techniques can contaminate the sample at the job site. During shipment and storage, volatile organics (particularly methylene chloride and fluorocarbons) can diffuse through the septum and into the sample. A trip blank prepared from reagent water and carried through the sampling and handling protocol will serve as a check on such contamination.

6.3 During analysis, contamination can come from impurities in the purge gas, or from organic compounds outgassing from the plumbing ahead of the trap where they were deposited by a previously analyzed high level sample. To reduce this, the use of non-Teflon plastic tubing, non-Teflon thread sealants, and flow controllers with rubber components in the purging device have been eliminated where possible.

6.4 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe is rinsed with reagent water between samples. Where practical, samples with unusually high concentrations should be followed by an analysis of reagent water to check for cross contamination. If the compounds present in high concentrations are also present is subsequent samples, the analyst must demonstrate that the positive results are not due to carryover by reanalysis of the samples. However, if the compounds are <u>not</u> present in the subsequent sample, then reanalysis is not necessary.

6.5 The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required. If the contamination is persistent, the complete purge and trap system should be purged first with 100°C reagent water, then, if necessary, with methanol. If methanol is used, either disconnect the trap or install a blank trap, as the methanol will adversely affect the trap's performance.

6.6 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

6.7 When using an ion trap, methanol content in blanks, standards, and samples should be kept as constant as possible because varying amounts of methanol can cause different spectra for certain compounds. (Chloroethane spectra does not look like reference spectra due to this phenomenon). **Maximum amount of methanol to be purged is 100 uL.**

7.0 SAFETY PRECAUTIONS

7.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the "TRIMATRIX Safety Manual".

7.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

7.3 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-dibromomethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Sample Collection

8.1.1 Collect all aqueous and liquid waste samples in duplicate 40 ml borosilicate glass screw-cap VOA vials with teflon lined silicone septa. Gently fill sample bottles to overflowing to minimize loss of volatiles. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Invert the vial the confirm that

there is no headspace present. If there is headspace or bubbles larger than 5-6 mm in diameter, refill a new preserved vial.

8.1.2 Collect soil/sludge/solid waste samples in accordance with USEPA Method 5035, as specified in TriMatrix SOP number GR-04-105 *Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples*, most current version.

8.2 Sample Preservation

8.2.1 Aqueous Samples

8.2.1.1 For aqueous samples, if the sample contains residual chlorine, collect the sample in a 125-ml container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40 ml VOA vial. Cool to 4°C and adjust pH to <2 with HCl. EPA Methods 330.4 and 330.5 may be used for measurements of residual chlorine. Field test kits are also available for this purpose.

8.2.1.2 TriMatrix Laboratories supplies all clientele with 40 ml VOA vials which are pre-preserved with HCl. If the vials were not supplied by the laboratory, and are not pre-preserved, fill vials and adjust the pH to <2 by carefully adding two drops of 1:1 HCl to each sample. Seal the sample bottle, PFTE-face down, and cool to 4 °C.

8.2.1.3 Samples collected for Acrolein and/or Acrylonitrile are to be preserved at a pH of 4-5 with 1:1 HCl or analyzed within 3 days of collection.

8.2.2 Soil/Sludge/Waste Samples

8.2.2.1 See section 8.1.2.

8.3 Trip Blanks - Aqueous Samples Only

8.3.1 A trip blank should accompany each sample set into the field and back. A sample set is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a pre-preserved sample bottle with reagent water, seal, and ship to the sampling site along with empty sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by the appropriate trip blank.

8.4 Sample Storage

8.4.1 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

8.4.2 Store samples at 4°C until analysis. The laboratory sample storage area must be free of organic solvent vapors. Soils/sludges/and wastes are stored separately from aqueous samples.

8.4.3 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be qualified as estimated.

8.4.4 If aqueous samples are unpreserved, hold time for aromatics is 7 days. Hold time for acrolein is 3 days.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Glassware and Hardware

9.1.1 Various size class A volumetric flasks. (10 mL, 50 mL, 100 mL, 250 mL, 1000 mL)

9.1.2 Various size microsyringes. (1 uL, 5 uL, 10 uL, 25 uL, 50 uL, 100 uL, 1000 uL)

9.1.3 5 mL gas tight luerlock syringes

9.1.4 60 or 125 mL wide mouth with Teflon-lined cap.

9.1.5 Borosilicate glass vials with teflon lined septum caps, 20 ml and 40 mL.

9.1.6 Various size teflon lined screw cap vials

9.1.7 refrigerator

9.1.8 pH test strips

9.1.9 metal spatulas

9.1.10 analytical balance 0.0001 g & top-loading balance - 0.01 g.

9.1.11 pasteur pipets (disposable) with rubber pipet bulb

9.2 Instrumentation

9.2.1 Concentrators (Other concentrators may be substituted if equivalent data can be produced.)

9.2.1.1 Dynatech Precision Sampling Dynasoil concentrator recommended conditions:

Trap: Supelco Vocarb 4000
preheat: 1 min. at 40°C
purge: 11 min. at 35-40 mL/min.
dry purge: 3 min.
desorb preheat: 225°C
desorb: 230°C for 2.0 min.
bake: 8 min. at 250°C
water trap: low = 38° C, high = 150°C
valve oven: 125°C
heated transfer line: 125°C

9.2.1.2 Tekmar LSC-2000 conentrator recommended conditions:

Trap: Supelco Vocarb 4000 (Carbopack/Cabosieve may also be used)
preheat: 1.0 min at 40°C
purge: 11 min. at 35-40 mL/min.
dry purge: 3 min.
desorb preheat: 245°C
desorb: 250° C for 2.0 min.
bake: 8 min. at 260°C
valve oven: 125°C
heated transfer line: 125°C

9.2.2 Autosamplers

- O. I. Analytical 4552 (Archon)
- Tekmar ALS 2016

- Dynatech PTA 30 W/S

9.2.3 Gas Chromatograph

9.2.3.1 Varian model 3400 temperature programmable gas chromatograph or equivalent equipped with a SPI injector and an Open Split Interface (OSI). Recommended conditions:

Injector Temperature: 150°C
Transfer Line Temperature: 250°C
OSI Temperature: 250°C
OSI Split Ratio: 20:1

Temperature Program: -10°C for 1 minute, then to 150°C at 6°C/min, then to 200°C at 15°C/min, hold at 200°C for 4-5 minutes.

9.2.3.2 Hewlett Packard Model 5890 Series II with a low dead volume injection port and glass jet separator. Recommended conditions:

Injector Temperature: 200°C
Transfer Line Temperature 280°C
Jet Separator Temperature: 250°C

Temperature Program: 35°C for 10 minutes, then 5°/min to 110°C, hold 1 minute, then 20°/min to 220°C, hold 2 minutes.

9.2.3.3 Hewlett Packard Model 5890 Series II equipped with electronic pressure control (EPC), a split/splitless injection port and a capillary direct interface.

Injector Temperature: 180°C
Transfer Line Temperature 280°C
EPC setting: Constant flow mode at 1.0 ml/min
Split Ratio: 40:1

Temperature Program: 35°C for 10 minutes, then 7°/min to 73°C, hold 1 minute, then 10°/min to 110°C, hold 1 minute, then 20°/min to 220°C, hold 2 minutes.

9.2.4 Columns:

9.2.4.1 75m x 0.53 mm ID, 3.0 um film thickness wide bore capillary column (J&W Scientific DB-624 or equivalent). Used in Varian 3400 (9.2.3.1).

9.2.4.2 75 m x 0.45 mm ID, 2.5 um film thickness, wide bore capillary column DB-VRX (J&W Scientific). Used in HP 5890 II with jet separator (9.2.3.2).

9.2.4.3 30 m x 0.25 mm ID, 1.4 um flim thickness, narrow bore capillary column DB-VRX (J&W Scientific). Used in HP 5890 II with capillary direct interface (9.2.3.3).

9.2.5 Mass Spectrometer (Saturn Ion Trap or Hewlett Packard 5971 MSD) capable of scanning from 35-650 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are purged onto the analytical column.

GC/MS recommended operating conditions:
Electron energy: 70 volts (nominal).
Mass range: 38-400 amu.
Scan time: 359 amu/second = 1 scan/sec.
Source temperature: 160 - 220°C

9.2.6 Data Acquisition

9.2.6.1 The Saturn data system is a DOS-based system that allows continuous acquisition and storage of all results obtained throughout the duration of each acquisition on hard disk. The software is able to process the data file and plot the ion abundance's of a specified mass versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The data files are then converted from Saturn files to HP files and processed using HP Enviroquant, an emvironmental data analysis software. The software also has a 75,000 compound NBS spectral library used in identifying unknown compounds.

9.2.6.2 The HP MSD data acquisition system is DOS-based HP Chemstation equipped with Enviroquant, an environmental data analysis software. It is also capable of plotting EICP's and has a 75,000 compound NBS spectral library.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 GC Maintenance

10.1.1 Change septa weekly or as needed.

10.1.2 Change gas scrubber traps yearly or as needed.

10.1.3 Clip or replace GC column as needed.

10.1.4 Check column head pressure daily.

10.1.5 Check gas cylinder pressure daily and change if needed.

10.2 Mass Spec Maintenance

10.2.1 Ion Trap Maintenance Change

10.2.1.1 Mechanical pump oil every 6 months.

10.2.1.2 Clean Ion Trap Analyzer at least annually.

10.2.1.3 Replace prefilled oil reservoir every 6 months.

10.2.1.4 Examine o-ring gasket seals and replace if necessary after analyzer maintenance.

10.2.1.5 Replace the electron multiplier as necessary

10.2.2 MSD Maintenance

10.2.2.1 Change rough pump oil every six months.

10.2.2.2 Check diffusion pump oil annually and change if discolored or low.

10.2.2.3 Clean ion source at least annually (maybe needed more frequently as shown by detector performance).

10.2.2.4 Examine & replace large o-ring seal if worn.

10.2.2.5 Replace electron multiplier as needed. (Maximum voltage 3000).

10.3 Purge and Trap

10.3.1 Bake out trap daily before use

10.3.2 Check purge flow weekly

10.3.3 Empty waste bottles and fill rinse bottles daily

10.3.4 Check concentrator pressures

10.3.5 Check and fill internal/surrogate standard syringe daily

11.0 CHEMICALS AND REAGENTS

11.1 Chemicals

11.1.1 Reagent water (organic free) ASTM Type II

11.1.2 Methanol (purge and trap grade)

11.1.3 Pure stock standard materials or certified stock standards (96% pure or greater)

11.1.4 1:1 Hydrochloric Acid

11.1.5 Polyethylene glycol - Free of interferences at the detection limit of the target analytes.

11.1.6 Sodium bisulfate, Na_2HSO_4, ACS reagent grade or equivalent.

12.0 STANDARDS PREPARATION

12.1 All standards used in the laboratory must be recorded in the standards logbook. Vendors, lot #'s, concentrations, purity's, etc. are recorded. Each standard is given a unique ID #.

12.2 Stock & Intermediate Standard Storage Requirements

12.2.1 Gas standards should be monitored closely for degradation. Stock standards for gases usually will need to be replaced after month. Intermediate gas standards usually will need to be replaced after one week. If the continuing calibration standard varies by more than 25% from the initial calibration curve, then a new gas standard needs to be prepared. The first compound to fail will generally be dichlorofluoromethane, so it's response should be monitored closely.

12.2.2 All other stock standards may be kept up to 12 months. Intermediate standards may be kept for up to 6 months; however, they should be continuously monitored for degradation by comparison of the response of the compounds in daily continuing calibration standards to that of the initial calibration curve.

12.2.3 2-Chloroethyl vinyl ether should be prepared separately from the other compounds due to its reactivity. Intermediate standards should be prepared fresh monthly.

12.2.4 All stock and intermediate standards are to be stored with minimal headspace at -10°C to -20°C.

12.3 Stock Standards

12.3.1 Stock Solutions may be prepared from pure standard materials or purchased as certified solutions. Commercially prepared stock standards can be used a. ny concentration if they are certified by the manufacturer or by an independent source.

12.3.2 If preparing stock standards from neat compounds no adjustment factor is needed when the chemical has greater than or equal to 96% purity. If the purity is less than 96% then an adjustment factor must be used. Prepare stock standard solution in methanol using assayed liquids. Transfer the stock standard solution into teflon sealed screw-cap bottles. Store in a freezer separate from samples and protect from light.

12.3.2.1 Gravimetric Method
10,000 mg/L stock standard: 0.5g of each analyte (neat) is injected into a 50 mL volumetric flask partially filled with methanol which has been tared on an analytical balance. The weight is recorded to the nearest 0.0001g the volumetric filled to the mark with methanol, capped and inverted three times to ensure proper mixing.

12.3.3 Commercial Stock Standards are purchased as custom mixtures from Accustandard Inc.

12.3.3.1 Standard IA: Volatile Organic Compounds - Liquids @ 2.0mg/mL in MeOH (Accustandard M502A-R-10X). See Table 2A.

12.3.3.2 Standard IB: Volatile Organic Compounds - Gases @ 2.0mg/mL in MeOH (Accustandard M502B-10X). See Table 2A.

12.3.3.3 Standard IC: Acrolein & Acrylonitrile @ 1.0 mg/mL in water (Accustandard M-603/M-001M).

12.3.3.4 Standard ID: 2-Chloroethyl Vinyl Ether @ 2.0 mg/mL in MeOH (Accustandard M-601C-10X).

12.3.3.5 Standard IE: Custom Additions to Method 8260 @ 2.0 mg/ml in MeOH (Accustandard S-3439-R1). See Table 2A.

12.3.3.6 Standard II: Appendix IX Standard @ 2.5 mg/mL in MeOH (Accustandard S-3651 Volatile Custom Solution). See Table 2B.

12.3.3.7 Standard III: Internal Standard/Surrogate Standard Mixture: These standards are purchased commercially at 2.0 mg/ml for the Ion Trap and at 5.0 mg/ml for the MSD's. The compounds are also different between the two instruments due to spectral interferences on the Ion Trap for the recommended 8260B internal and surrogate standards.

12.3.3.7.1 Internal Standards for Ion Trap (Ultra Scientific

12.3.3.7.1.1 Pentafluorobenzene

12.3.3.7.1.2 1,4-Difluorobenzene

12.3.3.7.1.3 Chlorobenzene-d5

12.3.3.7.1.4 1,4-Dichlorobenzene-d4

12.3.3.7.2 Surrogate Standards for Ion Trap (Ultra Scientific

12.3.3.7.2.1 Dibromofluoromethane

12.3.3.7.2.2 Toluene-d8

12.3.3.7.2.3 4-Bromofluorobenzene

12.3.3.7.3 Internal Standards for HP 5971 MSD (Ultra Scientific

12.3.3.7.3.1 Fluorobenzene

12.3.3.7.3.2 Chlorobenzene-d5

12.3.3.7.3.3 1,4-Dichlorobenzene-d4

12.3.3.7.4 Surrogate Standards for HP 5971 MSD (Ultra Scientific

12.3.3.7.4.1 Dibromofluoromethane

12.3.3.7.4.2 1,2-Dichloroethane-d4

12.3.3.7.4.3 Toluene-d8

12.3.3.7.4.4 4-Bromofluorobenzene

12.3.3.8 Standard IV: Standard Surrogate @ 2.0 mg/mL in MeOH (Ultra Scientific STM-330N).

12.4 Intermediate Standards - concentrations of working, surrogate, and internal standards are recommended and subject to change.

12.4.1 8260 Intermediate Standard: This standard will be at a concentration of 100 ug/mL. To make the 100 ug/mL standard add 50 uL of IA (12.3.3.1), IB (12.3.3.2), ID (12.3.3.4), and IE (12.3.3.5) to 800 uL of methanol.

12.4.2 Acrolein and Acrylonitrile Intermediate Standard: This standard will be at a concentration of 100 ug/mL. To make the 100 ug/mL standard, add 100 uL of IC (12.3.3.3) to 900 uL of methanol.

12.4.3 Appendix IX Intermediate Standard: This standard will be at a concentration of 250 ug/mL. To make the 250 ug/mL standard, add 100 uL of II (12.3.3.6) to 900 uL of methanol.

12.4.4 Surrogate Intermediate Standard A: This standard will be at a concentration of 50 ug/mL. To make the 50 ug/mL standard, add 25 uL of IV (12.3.3.8) to 975 uL of methanol. This standard will be used for the initial calibration curves.

12.4.5 Surrogate Intermediate Standards B: This standard will be at a concentration of 20 ug/ml. To make the 20 ug/ml standard, add 10 uL of IV (12.3.3.8) to 990 uL of methanol. The surrogate standard will be used for spiking methanol extracted samples.

12.4.6 Combined Intermediate Internal Standard/Surrogate Standard Mixture

12.4.6.1 If adding IS/SS standard manually, make a working standard by adding 1 mL of a 2.0 mg/mL commercially prepared standard III into a 3/4 full 100 mL volumetric flask. Add the standard directly to the methanol to prevent any loss of the volatile

compounds. Follow the same procedure for the commercially prepared surrogate standard solution. Dilute to volume with methanol, stopper, and invert 3 times. This will produce a working standard at 20 ug/mL. Transfer the solution to as many 1.5 mL auto sampler vials as possible and store in the freezer.

12.4.6.2 If the purge and trap auto sampler will add the IS/SS Standard automatically, prepare a working standard solution at 200 ug/mL by diluting 1 mL of the 5.0 mg/ml commercially prepared standard III into a 3/4 full 25 mL volumetric flask and dilute to volume. Store in the freezer.

12.5 Calibration and Calibration Check Standards are prepared in water in either a 50 mL volumetric flask or a 5 mL gas-tight syringe using the formula below. CCV standards are at 40 ug/L for all compounds excpet the Appendix IX compounds which are at 100 ug/L.:

12.5.1 Working standards are prepared in water in either a 50 mL volumetric or a 5 mL syringe using the formula below:

$$Vs = \frac{Cf\ Vf}{Cs}$$

where:

Vs = volume of stock to inject (uL)
Cf = final concentration of working std (ug/L)
Vf = final volume of working stds (uL)
Cs = concentration of stock (ug/L)

These Standards are prepared as needed and are not stored. See section 14.2.2

12.6 Matrix Spike Standards

12.6.1 Intermediate stock standards as prepared in section 12.4.1 are used for matrix spiking purposes. Matrix spikes are prepared using the formula given in section 12.5. The final concentration will be 40 ug/L.

12.6.2 For a quality control purposes, the following compounds are routinely reported: 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.

12.6.3 **For the State of Wisconsin samples, all analytes from the matrix spike standard are to be reported and compared to statistical control limits.**

12.7 Laboratory Fortified Blank (LFB) Standards

12.7.1 Intermediate stock standards as prepared in section 12.4.1 are generally used for laboratory fortified blanks. LFBs are prepared using the formula given in section 12.5. The final concentration will be 40 ug/L.

12.7.2 For routine quality control purposes, the following compounds are routinely reported: 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.

12.7.3 **For the State of Wisconsin samples, all analytes from the LFB standard are to be reported and compared to statistical control limits.**

12.8 Laboratory Control Sample (LCS) Standards

12.8.1 Intermediate stock standards as prepared in section 12.4 are used for Laboratory Control Samples. The analyst must use a different lot # standard than the one used for the calibration standards. The LCS standards are prepared as in 12.5 and are made using standards IA, IB, IC, ID and IE for a regular 8260B curve or using standard II for an appendix IX 8260B curve.

12.8.2 All initial calibration curve analytes are spiked into the LCS standard. For a complete list see Tables 1A and 1B. The concentrations are 40 ug/L for regular 8260 and 100 ug/L for Appendix IX.

13.0 SAMPLE PREPARATION

This section includes procedures beginning with removing sample from refrigeration until sample has been concentrated onto the sorbent trap.

13.1 Allow the sample to come to ambient temperature prior to introducing it to the syringe. If either the Dynatech PTA 30 or O.I. 4552 autosampler will be used for sample analysis, the sample will need no preparation - the 40 ml vial will be loaded directly into the autosampler. I the ALS 2016 or Dynasoils autosamplers will be used, remove the plunger from a 5 ml syringe. Open the sample bottle and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger. Vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, if only one sample vial has been provided, the analyst should immediately place the remaining sample in a 20 ml vial with no headspace, to be used if subsequent analysis is necessary. Pull back slightly on the plunger, spike 10 ul of the internal/surrogate standard solution (12.4.6.1) directly into the 5 ml syringe, and inject the sample into purging chamber.

13.1.1 For matrix spikes, if using Tekmar instruments, add 2 ul of the 100 ug/ml intermediate stock standard (12.4.1) in addition to the IS/SS standard If using a Dynatech or O.I. instrument, add 26 ul of the 100 ug/ml intermediate stock standard directly to a 40 ml vial. Refer to section 9.2.2 for recommended purge and trap conditions. Spiking amounts are subject to change.

13.2 Soil/Sludge and Waste Samples:

13.2.1 Low Concentration Method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. TriMatrix employs two methods for the low-level soils. The closed system purge and trap by EPA method 5035 is based on purging a heated 5 gram sample collected in a vial pre-preserved with a sodium bisulfate solution. This procedure is described in detail in TriMatrix SOP GR-04-105. The other method, based on the older 5030 method preparation is detailed below. It is based on purging a heated sample mixed with organic-free reagent water containing the internal/surrogate standard and, if applicable, matrix spiking standards. Analyze all blanks, spikes, standards, and samples under the same conditions as the samples.

13.2.1.1 Use a 5g sample if the expected concentration is <0.1 mg/kg or a 1g sample for expected concentrations between 0.1 and 1 mg/kg.

13.2.1.2 A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40° purge temperature.

13.2.1.3 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Section 13.2.1.1 into a tared purge device or autosampler vial. Note and record the actual weight to the nearest 0.1 g.

13.2.1.4 If a Dynatech PTA 30 or O.I. 4552 autosampler is to be used, then weigh out the soil directly into an autosampler vial. The autosampler will automatically add 5 ml of water, along with 1 ul of the IS/SS standard (12.4.6.2) to the sample container before purging. If a Tekmar ALS 2016 is to be used, remove the plunger from a 5 ml Luerlock type syringe and fill until overflowing with organic-free reagent water. Replace the plunger and compress the reagent water to vent trapped air. Adjust the volume to 5.0 ml. Pull back slightly on the plunger, and spike 10 ul of the IS/SS standard solution (12.4.6.1) directly into the 5 ml syringe.

13.2.1.4.1 For matrix spikes, if using Tekmar instruments, add 2 ul of the 100 ug/ml intermediate stock standard (12.4.1) in addition to the IS/SS standard If using a Dynatech or O.I. instrument, add 26 ul of the 100 ug/ml intermediate stock standard directly to a 40 ml vial. Refer to section 9.2.2 for recommended purge and trap procedures. Spiking amounts are subject to change.

13.2.1.5 After addition of the reagent water containing the IS/SS standard (and any matrix spike standards, if necessary), load the sample onto the purge and trap autosampler system.

NOTE: Prior to the attachment of the purge device, Sections 13.2.1.4 and 13.2.1.5 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

13.2.1.6 Fit the heating jacket over the purging device if using a Tekmar heated purge and trap unit. (The Dynatech autosampler uses a heated purging chamber.) Heat the sample to 40°C while purging. Refer to section 9.2.2 for recommended purge and trap procedures.

13.2.2 High Concentration Method: The method is based on extracting the soil/sludge with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e., petroleum and coke wastes) that are insoluble in methanol are diluted with polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water. This is purged at 40°C. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

13.2.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol, weigh 4g (wet weight) of sample into a tared 20 ml vial. Use a top loading balance. Note and record the actual weight to 0.1 gram. For waste that is soluble in methanol or PEG, weigh 1g (wet weight) into a tared scintillation vial or a 10 ml volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 ml of the appropriate solvent into the vial and mark the bottom of the meniscus. Discard this solvent.) Other solvents and procedures are covered in TriMatrix SOP number GR-04-105, *Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples*

13.2.2.2 For sediment/soil or solid waste, quickly add 9.0 ml of appropriate solvent; then add 1.0 ml of the surrogate standard (12.4.5) to the vial. For a solvent miscible sample, dilute the sample to 10 ml with the appropriate solvent after adding 1.0 ml of the surrogate standard (12.4.5). For matrix spikes, add 200 ul of the matrix spiking standard (12.4.1). Cap and shake for 2 min.

NOTE: Sections 13.2.2.1 and 13.2.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

13.2.2.3 After settling has occurred, transfer approximately 4 ml of the extract into a vial for storage, using a disposable pipet. The remainder may be discarded. These extracts should be stored at 4°C in the dark, prior to analysis.

13.2.2.4 For each batch of samples prepped the analyst must also prepare a Method Preparation Blank (MPB) and a Laboratory Fortified Blank (LFB). For the MPB, add 1.0 ml of the surrogate standard (12.4.5) to 9.0 ml of the appropriate solvent. For the LFB, use 0.2 ml of the matrix spiking(12.4.1) in addition to the surrogate standard and 8.0 ml of solvent.

13.2.2.5 If a screening procedure was followed, use the estimated concentration to determine the appropriate volume of methanol extract to add to the 5 ml of organic-free reagent water for analysis. Otherwise, estimate the concentration range of the sample from the low concentration analysis to determine the appropriate volume. If the sample was submitted as a high concentration sample, start with 100 ul. All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

13.2.2.6 Remove the plunger from a 5.0 ml Luerlock type syringe and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 ml. Pull the plunger back to 5.0 ml to allow volume for the addition of the sample extract. Add the volume of methanol extract determined in Section 13.2.2.5 and a volume of methanol solvent to total 100 ul (excluding methanol in standards). Inject 10 ul of internal standard (12.3.3.7.1). Inject sample into purging chamber. Refer to section 9.2.2 for recommended purge and trap procedures.

13.2.2.7 Analyze the MPB, LFB, and duplicate matrix spikes as in section 13.2.2.6.

14.0 CALIBRATION PROCEDURES

14.1 Tuning Criteria

14.1.1 No analysis of any kind may begin until 50 ng of 4-Bromofluorobenzene (BFB) injected onto the system produces a spectra that passes the tuning criteria given in Table 3.

14.1.2 The internal standard/surrogate mix as prepared in 12.4.6.1 contains 20 mg/L of 4-Bromofluorobenzene (BFB). Purging 2.5 uL of this standard in 5 mLs of reagent water puts 50 ng of BFB on column. BFB's must be the initial run every 12 hours for method 8260 and every 24 hours for method 624 before any samples, blanks or standards are run.

TABLE 3 BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

14.2 Initial Calibration

14.2.1 In addition to passing the BFB tuning criteria, a 5 point calibration curve must initially be run before any samples can be analyzed. A heated curve is required if low level heated soils are to be analyzed. **TriMatrix analyzes all standards and samples using a heated purge.** All target compounds and surrogates must be included in the 5 point curve including internal standards and surrogates.

14.2.2 For Dynasoils and Tekmar-ALS 2016 Autosamples remove the plunger from a 5 mL luer lock syringe. Fill the syringe with reagent water. Replace the syringe plunger and compress the sample. Tilt the syringe so the tip is in the air and vent any residual air while adjusting the sample volume to 5.0 mL. Pull back slightly on the plunger to create a small head space. Add 10 uL of internal standard standard spiking solution (12.4.6.1) through the tip of the syringe. Next, using a syringe, withdraw the volumes of standards specified in Tables 4A or 4B and add the aliquot directly to the 5 mL syringe through the tip. When discharging the contents of the

micro syringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water in the 5 mL syringe. Attach the syringe to the syringe valve on the purging device. Open the valve and inject the sample into the purging chamber. Close the valve. Start purging and data acquisition. Other concentration levels than those in Tables 4A and 4B may be analyzed. Note: a constant amount of internal standard is added to all standards, while surrogate concentration will vary. The second number in table 4A is the surrogate standard concentration in each standard.

14.2.3 For the Dynatech PTA 30 W/S Autosampler, prepare standards in 50 mL volumetric flasks using 10 times the amounts listed in Table 4 A&B. Transfer the sample to a 40 mL vial and load on the autosampler. The autosampler will take a 5 mL aliquot and add 1 uL of internal surrogate standard mixture before purging.

For soil samples and heated water samples, follow the same procedure only that a 5 mL aliquot of standard must be manually added to a 40 mL vial. Internal/surrogate standard will be automatically added before purging. All heated standards will be heated at 40°C.

14.2.4 Calculate Response Factors (RF's) for each compound using the quantitation ion, and the internal standard ion listed in Tables 5A or 5B. The RF is calculated as follows:

$$RF = \frac{A_x * C_{is}}{A_{is} * Cx}$$

where:
Ax = Area of the characteristic ion for the target compound.
Ais = Area of the characteristic ion for the specific internal standard.
Cx = Concentration of the compound being measured.
Cis = Concentration of the specific internal standard.

TABLE 4A
STANDARD 8260 VOLUMES REQUIRED FOR CURVE

Concentration of Working Std (ug/L 8260/Surr)	Volume (uL) of Standard (12.4.1)	Volume (uL) of Standard (12.4.2)	Volume (uL) of Standard III (12.4.6.1)	Volume (uL) of Standard IV (12.4.4)
10/80	0.5	0.5	10.0	4.0
20/70	1.0	1.0	10.0	3.0
40/40	2.0	2.0	10.0	---
100/60	5.0	5.0	10.0	2.0
200/50	10.0	10.0	10.0	1.0

*Note: For standard made-up 50 mL volumetric flasks, add 10 times the above amounts.

TABLE 4B
APPENDIX IX VOLUMES REQUIRED FOR CURVE

Concentration of Working Std (ug/L)	Volume (uL) of Standard (12.4.3)	Volume (uL) of Standard III (12.4.6.1)
25	0.5	10.0
50	1.0	10.0
100	2.0	10.0
250	5.0	10.0
500	10.0	10.0

14.2.5 For compounds not listed in Tables 5A or 5B, a major ion that is dissimilar to potential coeluting or interfering ions should be chosen as the quantitation ion. The internal standard chosen should be one that has a retention time closest to the compound being measured.

14.2.6 An average RF for all 5 points of the curve must be calculated for each compound. Five compounds are checked for a minimum average response factor. These are the System Performance Check Compounds (SPCC's). They are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum relative response factor for the SPCC's are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	>0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

This check is used to monitor compound instability and degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

14.2.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

14.2.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

14.2.6.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.

14.2.7 The Percent Relative Standard Deviation (% RSD) also must be calculated for all compounds. Using the RF's from the initial calibration, calculate the % RSD using the following formula:

$$\% \text{ RSD} = (SD/x) * 100$$

where

RSD = relative standard deviation.
x = mean of the five initial response factors for a compound.

SD = standard deviation of average RF's for a compound.

All compounds should have a % RSD of ≤ 15%. Six compounds are used as Calibration Check Compounds (CCC's): 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethyl benzene, vinyl chloride. These compounds **must** have a % RSD of ≤30%. If the % RDS is greater than 30 percent for any CCC, corrective action must be initiated and the system must be recalibrated.

14.2.8 If the % RSD of an non-CC compound is 15% or less, the relative response factor is assumed constant over the calibration range, and the average relative response factor may be used for quantitation.

14.2.9 If the % RSD of any non-CCC compound is greater than 15%, than the analyst must construct calibration curves of area ratio (Area analyte/Area-IS) verses concentration using first or higher order regression fit of the five calibration standards. The analyst should select the option which provides the least calibration error.

14.3 Continuing Calibration

14.3.1 Every 12 hours a 40 ug/L continuing calibration standard containing each compound being quantitated is run after the BFB (see section 14.1). If a calibration curve has just been run then the 40 ug/L standard from the curve will be used as the 12 hour standard. This is done to verify instrument sensitivity, and to confirm the initial calibration curve is still valid. The continuing calibration standard is verified similarly to the initial calibration curve, by checking the SPCC's and the CCC's. The run must be heated if performing low level heated soil analyses.

14.3.1.1 System Performance Check Compounds (SPCC's): This is the same check that is applied during the initial calibration. The response factor for the SPCC compounds must be as listed in 14.2.6 (See section 14.2.4 for response factor calcuLation.) If these minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

14.3.1.2 Calibration Check Compounds (CCC's): After the SPCC's are met, the CCC's are used to check the validity of the initial calibration. Calculate the percent drift using the following formula:

$$\% \text{ Drift} = (C_1 - C_c)/C_1 x100$$

where:

C_1 = Calibration Check Compound Standard concentration.
C_c = Measure concentration using selected quantitation method.

If the % Drift for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met then corrective action must be taken. This criterion **MUST** be met before sample analysis can begin. If the CCC compounds are not analytes of interest, then all target analytes must adhere to the less than 20% criteria.

14.3.1.3 The internal standard responses and retention times of the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds as compared to the 40 ug/L standard, the system must be inspected for malfunctions and corrections must be made as needed. If the area for any of the internal standards changes by a factor of two (-50% to + 100%) as compared to the 40 ug/L standard, the system must be inspected for malfunctions and corrections must be made as needed. When corrections are made, reanalysis of the samples analyzed while the system was malfunctioning are necessary.

13.4 Blank

13.4.1 After the BFB and the curve or continuing calibration has been run, a reagent water blank is required before any samples are analyzed showing that the analytical system is free from interferences and contaminaiton. The acceptance criteria for the instrument blank is that all analytes of interest must be below their minimum reporting limits for all samples to be analyzed in that analtyical batch, except for common lab contaminants (methylene chloride or acetone), which may be 5X the reporting limit.. At a minimum a blank is run every 12 hour shift. A blank will be run more frequently if contamination is suspected from a high level sample or if laboratory contamination is in question. The blank samples should be carried through all stages of the sample preparation and measurement steps, and will be spiked with internal standards and surrogates.

15.0 ANALYTICAL PROCEDURE

15.1 Sample Analysis

Desorb the sample onto the column which should be temperature programmed to separate the analytes of interest. Refer to section 9.2.1, 9.2.2, and 9.2.3 for recommended desorb, bake and column temperature settings.

15.2 If the response for any compounds exceeds the working range of the calibration curve, prepare a dilution of the sample.

15.2.1 Water Samples: Prepare a dilution of the sample from the aliquot in the 20 mL vial (or a second vial) in either a 5 mL syringe or a volumetric flask. Total volume purged must be 5 mL. Organic free water must be used for the dilution. Add 10 uL of the internal standard/surrogate spike mix (12.4.6.1) to the syringe. Inject into purge device and start purging and data acquisition. Alternatively, pour the contents into a 40 mL vial and load onto the PTA 30 W/S, which will automatically add IS/SS Standards.

15.2.2 Soil/Sludge/Waste Samples: Prepare a 1g sample (13.2.1.1) if the expected concentration will be within the linear range. If a larger dilution is needed prepare as in 13.2.2 or per EPA method 5035 as specified in TriMatrix SOP GR-04-105.

15.3 Qualitative Analysis:

15.3.1 The qualitative identification of compounds is based on retention time and comparison of sample mass spectra with standard mass spectra. The characteristic ions from the standard mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions are present.

15.3.2 All detected compounds must have a relative retention time (RRT) within ± 0.06 RRT units of the RRT of the standard component.

15.3.3 The relative intensities of the characteristics ions in the sample spectrum must agree within 30% of the relative intensities of these ions in the reference standard spectrum.

15.3.4 When there are resolution problems between compounds, mass spectral results will not give a true spectrum of either compound. When this occurs, examination of the extracted ion current profiles and possibly background subtraction, should be used to help identify whether or not the analytes are present.

16.0 CALCULATIONS AND DATA HANDLING

16.1 Aqueous Samples

16.1.1 Concentration of analyte is determined as follows:

$$\frac{A_x * C_{is}}{A_{is} * RF} * DF = ug/L$$

where:

Ax = Area of the characteristic ion for the target compound.
Ais = Area of the characteristic ion for the specific internal standard.
Cis = Concentration of the specific internal standard in ug/L.
RF = Average Response Factor.
DF = Dilution Factor.

16.1.2 Surrogate Recovery

$$\% \text{ Recovery} = \frac{Ax * Cis * DF * 100}{Ais * RF * TV}$$

TV = true value (40 for aqueous samples)

16.1.3 Matrix Spike Recovery

$$\% \text{ Recovery} = \frac{CS - CC}{TV} \text{ x } 100$$

CS = Concentration of sample plus spike (ug/L) as calculated in 16.1.1
CC = Concentration of sample (ug/L) as calculated in 16.1.1
TV = True value (40 for aqueous samples)

16.1.4 % Relative Percent Difference of MS/MSD

$$\% \text{ RPD} = \frac{Cms - Cmsd}{(Cms + Cmsd)/2} x100$$

Cms = Concentration of matrix spike as calculated in 16.1.1.
Cmsd = Concentration of matrix spike duplicate as calculated in 16.1.1.

16.2 Soil/Sludge/Waste (low concentration method)

16.2.1 Concentration of analyte is determined as follows:

$$\frac{mg}{kg} = \frac{Ax * C_{IS}}{A_{IS} * RF} * \frac{5ml}{W * \%S} * \frac{L}{1000ml} * \frac{mg}{1000ug} * \frac{1000g}{kg}$$

where:

Ax = Area of the characteristic ion for the target compound.
A_{IS} = Area of the characteristic ion for the specific internal standard.
C_{IS} = Concentration of the specific internal standard in ug/L.
RF = Average Response Factor
DF = Dilution Factor.
W = wet weight of sample (g)
% S = % solids in decimal form (i.e., 0.90 = 90% solid). Used to calculate dry weight results for soils and sludges only. See Modified EPA Method 160.3.

16.2.2 Surrogate Recovery

16.2.2.1 Calculate as in 16.1.2 if surrogate was added to the purge device or to syringe. (As prepped in section 13.2.1.)

16.2.3 Matrix Spike Recovery

$$\% \text{ Recovery} = \frac{CS - CC}{TV} \text{ x } 100$$

Where:

CS = concentration of sample plus spike (mg/kg) as calculated in 16.2.1.
CC = concentration of sample (mg/kg) as calculated in 16.2.1.
TV = true spike value corrected for % solids (generally 0.040 for solid samples prior to % solids correction.)

16.2.4 % Relative Percent Difference of MS/MSD

$$\% \text{ RPD} = \frac{Cms - Cmsd}{(Cms + Cmsd)/2} x100$$

Cms = Concentration of matrix spike as calculated in 16.2.1.
Cmsd = Concentration of matrix spike duplicate as calculated in 16.2.1.

16.3 Soil/Sludge and Waste (High Concentration Method):

16.3.1 Concentration of analyte is determined as follows:

$$\text{mg/kg} = \frac{Ax * C_{IS}}{A_{IS} * RF} * \frac{DF}{\%S} * \frac{V}{W} * \frac{L}{1000ml} * \frac{mg}{1000ug} * \frac{1000g}{kg}$$

Ax = area of the characteristic ion for the target compound
A_{IS} = area of the characteristic ion for the specific internal standard
C_{IS} = concentration of the specific internal standard in ug/L
RF = Average Response Factor
DF = dilution factor
V = volume of solvent added to sample during extraction or dilution (mL)
W = wet weight of sample extracted or diluted (g)
% S = % solids in decimal form (i.e., 0.90 = 90% solid). Used to calculate dry weight results for soils and sludges only. Wastes are calculated on a wet weight basis. See Modified EPA Method 160.3.

16.3.2 Surrogate Recovery

$$\%\ \text{Recovery} = \frac{A_x * C_{IS} * DF * 100}{A_{IS} * RF * TV}$$

TV = true value of surrogate spike

16.3.3 Matrix Spike Recovery

$$\%\ \text{Recovery} = \frac{CS - CC}{TV} \times 100$$

CS = concentration of sample plus spike (mg/kg) as calculated in 16.3.1.
CC = concentration of sample (mg/kg) as calculated in 16.3.1.
TV = true spike value corrected for % solids.

16.3.4 % Relative Percent Difference of MS/MSD

$$\% \text{ RPD} = \frac{Cms - Cmsd}{(Cms + Cmsd)/2} x100$$

Cms = Concentration of matrix spike as calculated in 16.3.1.
Cmsd = Concentration of matrix spike duplicate as calculated in 16.3.1.

16.4 Where applicable, use the regression line fitted to the initial calibration to determine the concentration of analytes.

16.5 Tentatively Identified Compounds (TIC's)
When requested, an estimate of concentration for analytes not present in the quantitation standard(s) will be made. The most recent release of the NIST/EPA/MSDC mass spectral library shall be used to identify TIC's. Compounds with responses less than 10% of the internal standard will not be reported. Relative intensities of the major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum. The relative intensities of the major ions should agree within +/-20%. (Example: For an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 30 and 70%.) MolecuLar ions present in the reference spectrum should be present in the sample spectrum. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. The formulas given in 16.1.1, 16.2.1, and 16.3.1 will be used to quantitate TIC's with the following modifications: The areas Ax and Ais should be from the total ion chromatogram, the internal standard used will be the closest in elution time to the unknown in the sample that is free of interferences, and the RF used will be 1. The concentration obtained will be reported indicating that the value is estimated. If no valid identification can be made then the compound should be reported as unknown aromatic, unknown hydrocarbon, etc.

17.0 DATA REPORTING AND DELIVERABLES

17.1 The analyst running a set of samples is responsible not only for the quality of the data results themselves, but also for filling out the correct documentation. It is important to document the analyses by correctly filling out, turning in, and filing the correct paperwork. This is required for quality control purposes, and in order to provide the client with defensible data.

17.2 LIMS Reporting

17.2.1 When the analyst has finished running a set of samples the data must be turned in to LIMS. The benchsheets must be filled in completely to insure that the results are reported correctly,

and the data is associated with the right quality control batch. It is important that the quality control batch number from the extraction summary, and the analytical batch information from the 24 hour shift are both filled in correctly. The dilution factor needs to be added if necessary so that the detection limits are raised accordingly. All positive hits should be added by crossing out the detection limit and writing down the final result that goes to the client on the right hand side of the detection limit. This is the result that has already been through all necessary calculations, including the dilution factor. If a dilution was made to the sample and there was a positive hit, the analyst also must include the new elevated detection limit for the analyte with the positive hit by writing it down to the left of the normal detection limit. Surrogates results are reported in amounts found in the extract, amount spiked in the extract, and percent recoveries.

17.2.2 If there are spikes, the quality control benchsheets must also be turned in. In addition to the requirements listed in Section 17.2.1, quality control benchsheets need the spiked amounts, percent recoveries, and percent differences where applicable. If out of control results are present due to extraction or severe matrix problems, the exclude (EXC) box should be checked to prevent the data from biasing the recovery window statistics.

17.2.3 A method blank (MPB) and a Laboratory Fortified Blank (LFB) must be turned in for every analytical batch. If running both 8021 and 601/602 samples, blank benchsheets must be turned in for each method. It is important to remember that a LFB cannot be turned in without first having turned in the associated MPB. A three digit extension (shift and date of the month - i.e. 115 for first shift on the 15th) will be assigned to each MPB and LFB, and this same extension will be added to all associated samples analyzed at the same time.

17.2.4 If internal chain-of-custody is required it is very important that the COC sheet is filled out correctly. All days that the analyst is in possession of the samples need to be accounted for.

17.2.5 All LIMS benchsheets (including the COC sheets) are to be placed in the correctly colored folders and turned into the data entry person responsible for entering the results. The blue folders containing the MPB's also should have the blank raw data quantitation reports and chromatograms included. All rush or past due projects should be in red or green folders.

17.3 Laboratory Required Paperwork

17.3.1 All run, maintenance, tape, and standard logbooks must be filled in completely and correctly. Corrections are to be made with a single lineout and then initialed and dated, not a writeover, and blank lines in the run logbook should be Z'd out, initialed and dated.

17.3.2 All ICV and CCV standard runs must be archived in their correct binders.

17.3.3 All LIMS documentation (except for the sample and quality control benchsheets), and the raw data (except for the blanks and what is listed in 17.3.2) should be placed in the correct folder and turned into the Volatile Laboratory technician who will record the date, time, and contents that were turned in.

17.4 Rounding and Significant Figures

17.4.1 Rounding is performed on the final quantitated result only. All non-quality control results are rounded to 2 significant figures.

17.4.2 Quality control results are rounded to 3 significant figures.

17.4.3 Percent recoveries and percent differences are reported as whole numbers up to 3 significant figures.

18.0 QUALITY ASSURANCE

18.1 BFB (Section 14.1)

18.2 5 Point Curve (Section 14.2)

18.3 Continuing Calibration Standard (Section 14.3)

18.4 Blank (Section 14.4)

18.5 Method Preparation Blank (MPB)

An MPB must be analyzed each day prior to running samples, and must have no positive results above the laboratory reporting limits for any analyte. If this requirement is not met, sample analysis may not begin, and corrective action must be performed. The only exception to this is for common laboratory contaminants (i.e. methylene chloride, acetone, and MEK), which may contain up to five times the laboratory reporting limit. However, any positive results reported for those analytes with concentrations between one and five times that reported in the blank will be qualified as estimated. If the samples to be analyzed are from methanol preparation, the MPB must contain 100 ul of methanol. If samples containing the bisulfate preservative are being analyzed, a MPB containing sodium bisulfate must also be analyzed.

18.6 Laboratory Fortified Blank (LFB)

A LFB is required with each 12 hour analytical batch, or every 20 samples, whichever is more frequent. It is taken from the results of the CCV at a mid-level concentration. The LFB serves as a check of method/extraction performance in the event that matrix spike recoveries are not within applicable control limits. Recoveries must be calculated and compared to LIMS control limits. Analysis must be stopped and the problem corrected if recoveries are outside the control limits. For aqueous and low level soil samples, the LFB may be either from the same source or separate source as the curve. For high level soils and wastes, see section 13.2.2.4 or TriMatrix SOP GR-04-105 (Method 5035) for LFB preparation procedures. Any sample analyzed in a batch with a failing LFB must be re-analyzed for the failing parameters. If this is not possible, all data must be qualified as estimated.

18.7 Matrix Spikes (MS, MSD)
Duplicate matrix spikes at a mid-level concentration are analyzed for each batch of 20 samples of the same matrix. Recoveries and % RSD are compared to statistically derived LIMS control limits. Recoveries/% RSD outside these limits must be qualified. (See TriMatrix Volatile Laboratory Corrective Actions SOP - GR-03-124.)

18.8 Spike Reporting

18.8.1 All routinely requested 8260B analytes listed in standards 1A & 1B will be added when spiking. All of these analytes will be reported at least twice each month for each matrix in order to generate quality control limits for all analytes.

18.8.2 For both LFB and matrix spikes, a list of 5 compounds is reported as follows for method 8260B. (This list is subject to client requests).

1. 1,1-Dichloroethylene
2. Trichloroethylene
3. Chlorobenzene
4. Benzene
5. Toluene

18.8.3 **For all State of Wisconsin samples, all of the spiked analytes will be reported when analyzing both LFB's and matrix spikes.**

18.9 Laboratory Control Sample (LCS)
After a new calibration curve is generated a separate source LCS must be analyzed for all target compounds. The windows are ± 25%. Analysis must be stopped and the problem corrected if recoveries are outside these windows.

18.10 Internal Standard Responses

18.10.1 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. The retention time for all internal standards must be within ± 30 sec from the last continuing calibration check standard. The EICP area for all internal standards must stay within a factor of two (-50% to +100%) from the last daily calibration standard check.

18.10.2 The EICP area for all internal standards in samples must stay within a factor of two (-50% to +100%) from the last daily calibration standard check.

18.10.3 If it appears that a sample matrix effect is causing a deviation, the sample will not be re-run. If there is no apparent reason for the deviation, then the sample will be re-run. If it works the second time, the second run will be reported. If it does not work this second time, a dilution of the sample will be performed until the internal standard meets criteria. Detection limits will be raised accordingly. If a dilution still does not meet criteria then all compounds associated with the internal standard that was out will be considered estimated. If many samples are out of control for no apparent reason, the mass spectrometer needs to be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning are necessary.

18.11 Surrogate Recoveries

18.11.1 All surrogates must fall within statistically derived LIMS control limits or method windows if LIMS windows are wider. If any surrogate compound is out of control due to obvious matrix problems, the sample will not be re-run and the sample will be qualified as estimated. If the sample has a surrogate that is out for no apparent reason, the sample will be re-run. If the re-run works, the first run will be discarded, and the second run reported. If many samples are out of control for no apparent reason, the mass spectrometer needs to be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, re analysis of samples analyzed while the system was malfunctioning are necessary.

18.11.2 If a high level sample is solvent extracted or diluted (13.2.2) and the true value of the surrogate is less than 8 ug/L, surrogate recoveries will not be reported.

18.12 Method 624 Modifications
This SOP was written primarily as method 8260B, however the following modifications are allowed for method 624.

18.12.1 The 12 hour shift is replaced by a 24 hour shift (14.1.2). BFB and a continuing calibration (14.3.1) standard are still required, only they are run every 24 hours instead of every 12.

18.12.2 A 3 point curve can be used in place of a 5 point curve (14.2.1).

18.12.3 SPCC's and CCC's are not used (14.2.5 and 14.2.6). Instead the RF's for every compound listed on the Method 624 list must have ≤35 % RSD for the curve to be valid.

18.12.4 The continuing calibration standard also does not use SPCC's and CCC's (14.3.1.1 and 14.3.1.2). The RF for every compound in the 40 ug/L continuing calibration standard is compared with the corresponding calibration acceptance criteria found in Table 6. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual RF falls outside the range, a new continuing calibration standard, or a new curve will be run.

18.12.5 There is no criteria for internal standard areas or retention times in Method 624. The Method 8260B criteria will be followed, but are not mandatory (18.10).

18.12.6 Every compound of interest that is on the Method 624 list must be in the matrix spikes, laboratory control samples, and LFB's, not just the limited list from 18.8.

18.12.7 Acrolein and Acrylonitrile may only be screened by GC/MS. All positive results must therefore be considered estimated.

19.0 ANALYST CERTIFICATION/METHOD VALIDATION

19.1 Before the analysis of any actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running a one time analyst certification. While the analyst certification is not instrument dependent, this certification is required on every instrument that will be running samples to demonstrate instrument ability to generate acceptable accuracy and precision.

19.2 Prepare a quality control check sample spiking standard at a level which will give concentrations at 20 ug/L per compound.

19.3 Analyze the four 1 ml samples following the SOP.

19.4 Calculate the average recovery (x) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

19.4.1 For each analyte x must be in the range 70-130% and s must be less than or equal to 20. If s and x for all analytes meet the acceptance criteria, the analyst certification is good. The analyst and the system are now authorized to run samples by this method. If any individual s

exceeds the precision limit or any individual falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

19.4.2 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to 19.5.

19.5 Locate and correct the source of the problem and repeat the test for all analytes that failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds beginning with Section 19.1. Samples may not be analyzed by any analyst or on any instrument until the analyst certification has been successfully completed. Copies of the successful analyst certifications/method validations spreadsheet and raw data should be given to the Quality Assurance Manager.

19.6 Method Detection Limit Studies

19.6.1 A Method Detection Limit (MDL) study must be performed for each analyte, for both waters and soils, to be quantitated by method 8260B1. All GC/MS instruments must perform MDL studies for each compound. Results obtained for analytes for which an MDL study has not been performed must be considered estimated. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. Actual Reporting Limits (RLs)are derived from the MDL study. RLs are the amount spiked for the MDL study provided that the MDL passed. The RL actually achieved in any given analysis will vary depending on instrument sensitivity, matrix effects, and dilutions.

19.6.2 The procedure followed for a MDL study is based on the method given in the Code of Federal Regulations, Part 136, Appendix B, 7-1-97, revision 1.11. All Method 8260B quality control procedures governing the analyses must be followed.

19.6.3 At least seven replicate analyses are performed using reagent water or sand, spiked with all analytes of interest, at the estimated RL concentration.

19.6.4 If the amount spiked is ≥1 and ≤5 times the calculated MDL, and there are no 0 percent recoveries in the set of seven, the MDL result is acceptable. If not the MDL must be re-run, only for the compounds that did not pass. If the study needs to be repeated at a different concentration, an entire set of seven needs to be re-run. If the study does not pass due to poor reproducibility on one of the samples, only that run needs to be re-analyzed.

20.0 REFERENCES

20.1 USEPA, SW846, Update III, Revision 2, 3rd Edition, Method 8260B, December 1996.

20.2 USEPA 40 CFR Method 624, Pt. 136, App. A., 1997.

20.3 USEPA CLP - Statement of Work, August 1991 Revision, Section IV.

21.0 ATTACHMENTS/APPENDICES

Approved By: _____ 5/28/98
QA Manager

Approved By: _____ 5/28/98
Area Manager

TABLE 1A
COMPOUND LIST, CAS#, AND REPORTING LIMITS FOR STANDARD I

Compound	CAS#	Aqueous DL (ug/L)	Soil DL (mg/kg)
Acetone	67-64-1	50	0.10
Acrolein	107-02-8	5.0	0.010
Acrylonitrile	107-13-1	1.0	0.010
Benzene	71-43-2	1.0	0.010
Bromobenzene	108-86-1	1.0	0.010
Bromochloromethane	74-97-5	1.0	0.010
Bromodichloromethane	75-27-4	1.0	0.010
Bromoform	75-25-2	1.0	0.010
Bromomethane	74-83-9	1.0	0.010
Carbon DisuLfide	75-15-0	5.0	0.10
Carbon Tetrachloride	56-23-5	1.0	0.010
Chlorobenzene	108-90-7	1.0	0.010
Chloroethane	75-00-3	1.0	0.010
2-Chloroethyl Vinyl Ether	110-75-8	10	0.10
Chloroform	67-66-3	1.0	0.010
Chloromethane	74-87-3	1.0	0.010
2-Chlorotoluene	95-49-8	1.0	0.010
4-Chlorotoluene	106-43-4	1.0	0.010
cis-1,2-Dichloroethylene	156-59-2	1.0	0.010
cis-1,3-Dichloropropylene	10061-01-5	1.0	0.010
Dibromochloromethane	124-48-1	1.0	0.010
1,2-Dibromo-3-Chloropropane	96-12-8	1.0	0.010
1,2-Dibromoethane	106-93-4	1.0	0.010

TABLE 1A
COMPOUND LIST, CAS#, AND REPORTING LIMITS
FOR STANDARD I
(Continued)

Compound	CAS#	Aqueous DL (ug/L)	Soil DL (mg/kg)
Dibromomethane	74-95-3	1.0	0.010
1,2-Dichlorobenzene	95-50-1	1.0	0.010
1,3-Dichlorobenzene	541-73-1	1.0	0.010
1,4-Dichlorobenzene	106-46-7	1.0	0.010
Dichlorodifluoromethane	75-71-8	1.0	0.010
1,1-Dichloroethane	75-34-3	1.0	0.010
1,2-Dichloroethane	107-06-2	1.0	0.010
1,1-Dichloroethylene	75-35-4	1.0	0.010
Dichlorofluoromethane	73-43-4	1.0	0.010
1,2-Dichloropropane	78-87-5	1.0	0.010
1,3-Dichloropropane	142-28-9	1.0	0.010
2,2-Dichloropropane	594-20-7	1.0	0.010
1,1-Dichloropropylene	563-58-6	1.0	0.010
Ethyl Ether	60-29-7	10	0.10
Ethylbenzene	100-41-4	1.0	0.010
Heptane	142-82-5	10	0.10
Hexachlorobutadiene	87-68-3	5.0	0.050
2-Hexanone	591-78-6	50	0.10
Iodomethane	74-88-4	1.0	0.010
Isobutyl acetate	110-19-0	10	0.10
Isopropanol	67-63-0	50	0.40

TABLE 1A
COMPOUND LIST, CAS#, AND REPORTING LIMITS
FOR STANDARD I
(Continued)

Compound	CAS#	Aqueous DL (ug/L)	Soil DL (mg/kg)
Isopropylbenzene	98-82-8	1.0	0.010
Methyl Ethyl Ketone (2-Butanone)	78-93-3	50	0.10
4-Methyl-2-Pentanone (MIBK)	108-10-1	50	0.10
Methyl tert-Butyl Ether (MTBE)	1634-04-4	50	0.10
Methylene Chloride	75-09-2	1.0	0.010
n-Butyl acetate	123-86-4	10	0.020
n-Butylbenzene	104-51-8	1.0	0.010
n-Propylbenzene	103-65-1	1.0	0.010
Naphthalene	91-20-3	5.0	0.050
p-Isopropyltoluene	99-87-6	1.0	0.010
sec-Butylbenzene	135-98-8	1.0	0.010
Styrene	100-42-5	1.0	0.010
tert-Butylbenzene	98-06-6	1.0	0.010
1,1,1,2-Tetrachloroethane	630-20-6	1.0	0.010
1,1,2,2-Tetrachloroethane	79-34-5	1.0	0.010
Tetrachloroethylene	127-18-4	1.0	0.010
Toluene	108-88-3	1.0	0.010
Trans-1,2-Dichloroethylene	156-60-5	1.0	0.010
Trans-1,3-Dichloropropylene	10061-02-6	1.0	0.010
1,2,3-Trichlorobenzene	87-61-6	1.0	0.010
1,2,4-Trichlorobenzene	120-82-1	1.0	0.010

TABLE 1A
COMPOUND LIST, CAS#, AND REPORTING LIMITS
FOR STANDARD I
(Continued)

Compound	CAS#	Aqueous DL (ug/L)	Soil DL (mg/kg)
1,1,1-Trichloroethane	71-55-6	1.0	0.010
1,1,2-Trichloroethane	79-00-5	1.0	0.010
Trichloroethylene	79-01-6	1.0	0.010
Trichlorofluoromethane	75-69-4	1.0	0.010
1,2,3-Trichloropropane	96-18-4	1.0	0.010
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	1.0	0.010
1,2,4-Trimethylbenzene	95-63-6	1.0	0.010
1,3,5-Trimethylbenzene	108-67-8	1.0	0.010
Vinyl Acetate	108-05-4	5.0	0.10
Vinyl Chloride	75-01-4	1.0	0.010
m,p-Xylene	999-99-9*	2.0	0.020
o-Xylene	95-47-6	1.0	0.010
Xylene, Total	1330-20-7	3.0	0.030
trans-1,4-Dichloro-2-butylene	110-57-6	5.0	0.050

*m-xylene 108-38-3
*p-xylene 106-42-3

TABLE 1B
COMPOUND LIST, CAS #, AND REPORTING LIMITS FOR STANDARD II

Compound	CAS#	Aqueous DL (ug/L)	Soil DL (mg/kg)
Acetonitrile	75-05-8	10	0.10
2-Butanol	15892-23-6	50	0.50
n-Butanol	71-36-3	40	0.23
t-Butanol	75-65-0	50	0.50
Cyclohexane	110-82-7	10	0.10
Cyclohexanone	108-94-1	50	0.10
2,3-Dichloro-1-propylene	78-88-6	1.0	0.010
1,2-Diethylbenzene	135-01-3	5.0	0.050
1,3-Diethylbenzene	141-93-5	5.0	0.050
1,4-Diethylbenzene	105-05-5	5.0	0.050
Dimethyl disuLfide	624-92-0	5.0	0.050
1,4-Dioxane	123-91-1	300	3.0
Ethanol	64-17-5	100	1.0
Ethyl Acetate	141-78-6	50	0.50
Hexachloroethane	67-72-1	5.0	0.050
Hexane	110-54-3	10	0.10
Isobutanol	78-83-1	50	0.50
Isopropyl ether	108-20-3	5.0	0.050
Methacrylonitrile	126-98-7	50	0.50
Methylcyclohexane	108-87-2	10	0.10
Methylcyclopentane	96-37-7	10	0.10
2-Nitropropane	79-46-9	10	0.10
n-Propanol	71-23-8	100	1.0
Propionitrile	107-12-0	50	0.50
trans-1,4-Dichloro-2-butylene	110-57-6	5.0	0.050

Approved By: [signature] 5/28/98 **Approved By:** [signature] 5/28/98
QA Manager **Area Manager**

TABLE 1B
COMPOUND LIST, CAS #, AND REPORTING LIMITS
FOR STANDARD II (continued)

Compound	CAS#	Aqueous DL (ug/L)	Soil DL (mg/kg)
Epichlorohydrin	106-89-8	5.0	0.010
Isobutyl acetate	110-19-0	10	0.10
Methyl Methacrylate	80-62-6	100	1.0
Tetrahydrofuran	109-99-9	10	0.10
n-Butyl acetate	123-86-4	10	0.020
Allyl Chloride	107-05-1	5.0	0.050

TABLE 2A
8260 STANDARD I COMPOUNDS AND CONCENTRATIONS

STD	Compound	Conc. (ug/mL)
IE	Acetone	100
IC	Acrolein**	100
IC	Acrylonitrile**	100
IA	Benzene	100
IA	Bromobenzene	100
IA	Bromochloromethane	100
IA	Bromodichloromethane	100
IA	Bromoform	100
IB	Bromomethane*	100
IE	Carbon DisuLfide	100
IA	Carbon Tetrachloride	100
IA	Chlorobenzene	100
IB	Chloroethane*	100
ID	2-Chloroethyl Vinyl Ether	100
IA	Chloroform	100

TABLE 2A
8260 STANDARD I COMPOUNDS AND CONCENTRATIONS
(Continued)

STD	Compound	Conc. (ug/mL)
IB	Chloromethane*	100
IA	2-Chlorotoluene	100
IA	4-Chlorotoluene	100
IA	cis-1,2-Dichloroethylene	100
IA	cis-1,3-Dichloropropylene	100
IA	Dibromochloromethane	100
IA	1,2-Dibromo-3-Chloropropane	100
IA	1,2-Dibromoethane	100
IA	Dibromomethane	100
IA	1,2-Dichlorobenzene	100
IA	1,3-Dichlorobenzene	100
IA	1,4-Dichlorobenzene	100
IB	Dichlorodifluoromethane*	100
IA	1,1-Dichloroethane	100
IA	1,2-Dichloroethane	100
IA	1,1-Dichloroethylene	100
IA	Dichlorofluoromethane*	100
IA	1,2-Dichloropropane	100
IA	1,3-Dichloropropane	100
IA	2,2-Dichloropropane	100
IA	1,1-Dichloropropylene	100
IE	Ethyl Ether	100

TABLE 2A
8260 STANDARD I COMPOUNDS AND CONCENTRATIONS
(Continued)

STD	Compound	Conc. (ug/mL)
IA	Ethylbenzene	100
IE	Heptane	100
IA	Hexachlorobutadiene	100
IE	2-Hexanone	100
IE	Iodomethane	100
	Isobutyl acetate	100
IE	Isopropanol	100
IA	Isopropylbenzene	100
IE	Methyl Ethyl Ketone (2-Butanone)	100
	Methyl Methacrylate	100
IE	4-Methyl-2-Pentanone (MIBK)	100
IE	Methyl tert-Butyl Ether (MTBE)	100
IA	Methylene Chloride	100
	n-Butyl acetate	100
IA	n-Butylbenzene	100
IA	n-Propylbenzene	100
IA	Naphthalene	100
IA	p-Isopropyltoluene	100
IA	sec-Butylbenzene	100

TABLE 2A
8260 STANDARD I COMPOUNDS AND CONCENTRATIONS
(Continued)

STD	Compound	Conc. (ug/mL)
IA	Styrene	100
IA	tert-Butylbenzene	100
IA	1,1,1,2-Tetrachloroethane	100
IA	1,1,2,2-Tetrachloroethane	100
IA	Tetrachloroethylene	100
IA	Toluene	100
IA	Trans-1,2-Dichloroethylene	100
IA	Trans-1,3-Dichloropropylene	100
IA	1,2,3-Trichlorobenzene	100
IA	1,2,4-Trichlorobenzene	100
IA	1,1,1-Trichloroethane	100
IA	1,1,2-Trichloroethane	100
IA	Trichloroethylene	100
IB	Trichlorofluoromethane	100
IA	1,2,3-Trichloropropane	100
IE	1,1,2-Trichloro-1,2,2-trifluoroethane	100
IA	1,2,4-Trimethylbenzene	100
IA	1,3,5-Trimethylbenzene	100
IE	Vinyl Acetate	100
IB	Vinyl Chloride*	100
IA	m,p-Xylene	200
IA	o-Xylene	100
IA	Xylene, Total	300

TABLE 2B
8260 APPENDIX IX COMPOUNDS AND CONCENTRATIONS

Compound	Conc. (ug/mL)
Acetonitrile	250
sec-Butanol	250
1-Butanol	250
t-Butanol	250
Allyl Chloride	250
Cyclohexanone	250
2,3-Dichloro-1-propene	250
Epichlorohydrin	250
p-Dioxane	250
Ethanol	250
Ethyl Acetate	250
Hexachloroethane	250
n-Hexane	250
Isobutyl Alcohol	250
Isopropyl Ether	250
Methacrylonitrile	250
2-Nitropropane	250
Propionitrile	250
1-Propanol	250
Tetrahydrofuran	250

TABLE 5A
ELUTION ORDER, QUANTITATION AND CHARACTERISTIC IONS, INTERNAL STANDARDS, AND SURROGATES FOR STANDARD I

Compound	Quantitation Ion	Secondary Ion(s)	Internal Standard
Dichlodifluoromethane	85	87, 50	1
Chloromethane	50	52, 49	1
Vinyl Chloride	62	64, 47	1
Bromomethane	94	96, 93	1
Chloroethane	45	43	1
Trichlorofluoromethane	101	103, 105	1
Dichlorofluoromethane	67	69, 47	1
Ethyl Ether	45	59, 73	1
Acrolein	55	56, 53	1
1,1-Dichloroethylene	96	61, 98	1
1,1,2-Trichloro-1,2,2-trifluoroethane	101	103, 151	1
Iodomethane	142	127, 141	1
Carbon DisuLfide	76	78, 77	1
Acetone	43	58, 42	1
Allyl Chloride	76	39, 41	1
Isopropanol	45	59, 43	1
Methylene Chloride	49	51, 84	1
Acrylonitrile	52	54, 53	1
Trans-1,2-Dichloroethylene	96	61, 98	1

TABLE 5A
ELUTION ORDER, QUANTITATION AND CHARACTERISTIC IONS, INTERNAL STANDARDS, AND SURROGATES FOR STANDARD I
(Continued)

Compound	Quantitation Ion	Secondary Ion(s)	Internal Standard
Methyl tert-Butyl Ether (MTBE)	73	43, 57	1
1,1-Dichloroethane	63	65,83	1
Vinyl Acetate	43	42, 44	1
2,2-Dichloropropane	77	41, 79	1
cis-1,2-Dichloroethylene	96	61, 63	1
Methyl Ethyl Ketone (2-Butanone)	43	72, 57	1
Bromochloromethane	49	130, 128	1
Tetrahydrofuran	71	41, 42	1
Chloroform	83	85, 47	1
1,1,1-Trichloroethane	97	99, 61	1
SUR:Dibromofluoromethane	113	111, 192	1
IS:Pentafluorobenzene	137	168, 99	1
Carbon Tetrachloride	117	119, 121	2
1,1-Dichloropropylene	75	110, 77	2
Benzene	78	51, 50	2
1,2-Dichloroethane	62	64, 49	2
Heptane	41	57, 71	2
IS:1,4-Difluorobenzene	114	88, 63	2
Trichloroethylene	130	95, 132	2
1,2-Dichloropropane	63	62, 76	2
Dibromomethane	93	95, 174	2
Methyl Methacrylate	41	69, 100	2
Bromodichloromethane	83	85, 129	2
2-Chloroethyl Vinyl Ether	63	65, 106	2

TABLE 5A
ELUTION ORDER, QUANTITATION AND CHARACTERISTIC IONS, INTERNAL STANDARDS, AND SURROGATES FOR STANDARD I
(Continued)

Compound	Quantitation Ion	Secondary Ion(s)	Internal Standard
Epichlorohydrin	49	57, 62	2
cis-1,3-Dichloropropylene	75	77, 110	2
4-Methyl-2-Pentanone (MIBK)	43	58, 85	2
SUR:d8-Toluene	98	100,70	2
Toluene	91	92, 65	2
n-Butyl acetate	43	56, 57	2
Trans-1,3-Dichloropropylene	75	77, 110	2
Ethyl methacrylate	41	99, 69	2
1,1,2-Trichloroethane	97	83, 85	2
Tetrachloroethylene	166	129, 168	3
1,3-Dichloropropane	76	78, 41	3
2-Hexanone	43	58, 85	3
Isobutyl acetate	43	41, 56	3
Dibromochloromethane	129	127, 131	3
1,2-Dibromoethane	109	107, 188	3
IS:d5-Chlorobenzene	82	117, 119	3
Chlorobenzene	112	77, 114	3
1,1,1,2-Tetrachloroethane	131	133, 119	3
Ethylbenzene	91	106, 51	3
m,p-Xylene	91	106, 51	3
o-Xylene	91	106, 51	3
Styrene	104	78, 51	3
Bromoform	173	175, 79	3
Isopropylbenzene	105	120, 79	4

TABLE 5A
ELUTION ORDER, QUANTITATION AND CHARACTERISTIC IONS, INTERNAL STANDARDS, AND SURROGATES FOR STANDARD I
(Continued)

Compound	Quantitation Ion	Secondary Ion(s)	Internal Standard
SUR:4-Bromofluorobenzene	95	174, 176	3
Bromobenzene	77	156, 158	4
1,1,2,2-Tetrachloroethane	83	85, 95	4
1,2,3-Trichloropropane	75	49, 110	4
n-Propylbenzene	91	120, 65	4
2-Chlorotoluene	126	91, 63	4
1,3,5-Trimethylbenzene	105	120, 77	4
4-Chlorotoluene	91	126, 63	4
tert-Butylbenzene	119	91, 134	4
1,2,4-Trimethylbenzene	105	120, 77	4
sec-Butylbenzene	105	134, 91	4
1,3-Dichlorobenzene	146	111, 148	4
p-Isopropyltoluene	119	134, 91	4
IS:d4-1,4-Dichlorobenzene	152	150	4
1,4-Dichlorobenzene	146	111, 148	4
1,2-Dichlorobenzene	146	111, 148	4
n-Butylbenzene	91	92, 134	4
1,2-Dibromo-3-Chloropropane	75	155, 157	4
1,2,4-Trichlorobenzene	180	182, 145	4
Hexachlorobutadiene	225	227, 260	4
Naphthalene	128	102, 51	4
1,2,3-Trichlorobenzene	180	182, 145	4

TABLE 5B
ELUTION ORDER, QUANTITATION AND CHARACTERISTIC IONS, FOR STANDARD II

Compound	Quantitation Ion	Secondary Ion(s)	Internal Standard
Ethanol	45	43	1
Acetonitrile	41	40, 54	1
t-Butanol	59	41, 43	1
Hexane	41	56, 57	1
Isopropylether	45	69, 86	1
n-Propanol	42	59, 41	1
Methylcyclopentane	56	41, 69	1
Propionitrile	54	52, 56	1
Ethyl Acetate	43	61, 45	1
Methacrylonitrile	67	41, 52	1
2-Butanol	45	59, 57	1
Sur: Dibromofluoromethane	113	111, 79	1
Cyclohexane	41	39, 57	1
IS: Pentafluorobenzene	137	168, 99	1
Isobutanol	41	43, 42	2
IS: 1,4-Difluorobenzene	114	88, 63	2
n-Butanol	41	39, 56	2
Methylcyclohexane	55	83, 98	2
2,3-Dichloro-1-propylene	75	77, 110	2
1,4-Dioxane	88	57, 43	2
2-Nitropropane	41	43, 46	2
Hexachloroethane	117	119, 201	2
Dimethyl disuLfide	45	79, 94	2
Sur: d-8-Toluene	98	100, 70	2
IS: d5-Chlorobenzene	82	117, 119	3
Cyclohexanone	55	42, 98	3

TABLE 5B
ELUTION ORDER, QUANTITATION AND CHARACTERISTIC IONS, FOR STANDARD II
(Continued)

Compound	Quantitation Ion	Secondary Ion(s)	Internal Standard
Sur: 4-Bromofluorobenzene	95	174, 176	3
trans-1,4-Dichloro-2-butylene	53	75, 89	4
IS: d4-1,4-Dichlorobenzene	152	150	4
1,3-Diethylbenzene	105	119, 134	4
1,4-Diethylbenzene	105	119, 134	4
1,2-Diethylbenzene	105	119, 134	4

TABLE 6
CALIBRATION AND QC ACCEPTANCE CRITERIA
METHOD 624

Parameter	Range for Q (ug/L)
Benzene	12.8-27.2
Bromodichloromethane	13.1-26.9
Bromoform	14.2-25.8
Bromomethane	2.8-37.2
Carbon tetrachloride	14.6-25.4
Chlorobenzene	13.2-26.8
Chloroethane	7.6-32.4
2-Chloroethylvinyl ether	D-44.8
Chloroform	13.5-26.5
Chloromethane	D-40.8
Dibromochloromethane	13.5-26.5
1,2-Dichlorobenzene	12.6-27.4
1,3-Dichlorobenzene	14.6-25.4
1,4-Dichlorobenzene	12.6-27.4
1,1-Dichloroethane	14.5-25.5
1,2-Dichloroethane	13.6-26.4
1,1-Dichloroethylene	10.1-29.9
trans-1,2-Dichloroethylene	13.9-26.1
1,2-Dichloropropane	6.8-33.2
cis-1,3-Dichloropropylene	4.8-35.2
trans-1,3-Dichloropropylene	10.0-30.0
Ethyl benzene	11.8-28.2
Methylene chloride	12.1-27.9
1,1,2,2-Tetrachloroethane	12.1-27.9

Approved By: 5/28/98 **Approved By:** 5/28/98
QA Manager **Area Manager**

TABLE 6
CALIBRATION AND QC ACCEPTANCE CRITERIA
METHOD 624
(Continued)

Parameter	Range for Q (ug/L)
Tetrachloroethylene	14.7-25.3
Toluene	14.9-25.1
1,1,1-Trichloroethane	15.0-25.0
1,1,2-Trichloroethane	14.2-25.8
Trichloroethylene	13.3-26.7
Trichlorofluoromethane	9.6-30.4
Vinyl chloride	0.8-39.2

D=Detected result must be greater than zero.

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

SEMI-VOLATILE LABORATORY ION TRAP MASS SPECTROMETRY ANALYSES OF BASE/NEUTRAL/ACID COMPOUNDS

MODIFIED METHODS 8270C AND 625

UNCONTROLLED DOCUMENT

APPROVALS:

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By: Janet M. Kudirka

Total Number of Pages: 45

1.0 SCOPE AND APPLICATION

1.1 Method 8270C is used to determine the concentration of semi-volatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8270C is used to quantify most basic, neutral, and acidic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic using a fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for target compounds, retention times, quantitation and secondary ions, internal standards and surrogates typically included in a Method 8270C analysis. Table 1A provides additional Appendix IX and other analytes covered by this method.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Its chromatography must be monitored for peak broadening. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. 1,2-diphenylhydrazine also decomposes in the injection port into azobenzene. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with a high boiling material.

1.4 The default quantitation limits for clean samples extracted from both 1000 mL or 30 g of sample, concentrated to 10 ml, and analyzed by Method 8270C are given in Table 2 and 2A. Quantitation limits will be proportionately higher depending on sample matrix and preparation method, and for sample extracts that require dilution.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method (see section 19).

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition*, Final Update III, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry", Revision 3, December 1996.

2.2 *40 Code of Federal Regulations, most current edition*, Pt. 136, App. A, Method 625-Base/Neutrals and Acids.

3.0 SUMMARY OF PROCEDURE

3.1 Prior to using this method, the samples should be prepared for analysis using the appropriate sample preparation and cleanup methods. Waters will be extracted using Modified EPA method 3510C, and soils by Modified EPA Method 3550B. This SOP describes the analysis of the resulting extract.

3.2 This SOP will be used as the default Method for all mass spectrometry ion trap semi-volatile analyses. It has been written to follow Method 8270C as closely as possible, and has been customized to cover the equipment and techniques being used at TriMatrix Laboratories, Inc., Grand Rapids, Michigan.

3.3 Wastewater samples will use the following Method 625 modifications.

3.3.1 The 12 hour shift is replaced by a 24 hour shift. DFTPP and a continuing calibration standard are analyzed once every 24 hours instead of every 12.

3.3.2 A 3 point curve can be used in place of a 5 point curve. SPCCs and CCCs are not used. Instead the RFs for every compound of interest listed on the Method 625 list must have <35% RSD for the curve to be valid.

3.3.3 The continuing calibration standard also does not use SPCCs and CCCs. The RF for every compound of interest in the continuing calibration standard that is on the 625 list must be ≤ 20% difference when compared against the curve. If not, either a new continuing calibration standard will be run with acceptable percent differences, or a new 3 or 5 point curve must be run.

3.3.4 There are no criteria for internal standard areas or retention times in Method 625. The Method 8270C criteria will be followed.

3.3.5 Every compound of interest that is on the Method 625 list (Method 625 Table 6) must be in the matrix spikes and the laboratory fortified blanks, not just the limited list specified in Method 8270C. Laboratory generated windows for spike recoveries are calculated as specified in the 8270C SOP. Additionally requested compounds are not spiked.

4.0 PARAMETER OR COMPOUND LIST

4.1 Analytes available for analysis by Method 8270C are listed in Table 1 and 1A. Other analytes may be run by this method provided they have been developed following the guidelines in this SOP

5.0 REFERENCED SOPs

5.1 TriMatrix Laboratories SOP #GR-09-101, *The Extraction of BNAs in Water*, latest version.

5.2 TriMatrix Laboratories SOP #GR-09-103, *Extraction of Semi-Volatile BNAs in Soil, Sediment and Sludge*, latest version.

5.3 TriMatrix Laboratories SOP #GR-04-101, *Semivolatile Laboratory Mass Spectrometry Corrective Actions*, latest version.

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Rinsing all washed glassware with pesticide quality or better methylene chloride immediately prior to use, as well as the use of high purity reagents and solvents helps to minimize interference problems.

6.2 Contamination can be caused whenever highly concentrated samples are followed by low or non-detect samples. This phenomenon is called carryover. To reduce carryover, the auto sampler syringe is washed multiple times between samples. Whenever possible, the analyst should analyze a reagent blank immediately after a high level sample. If carryover is suspected, all affected samples should be re-analyzed.

6.3 Corrective actions are outlined in TriMatrix Laboratories SOP #GR-04-101, *Semivolatile Laboratory Mass Spectrometry Corrective Actions*, latest version.

7.0 SAFETY PRECAUTIONS

7.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the TriMatrix Laboratories, Inc. Laboratory Safety Manual.

7.2 Methylene chloride and most of the target analytes, surrogates, and spikes, are highly toxic and cancer suspects. Wear appropriate protective clothing and gloves to avoid contact. Prepare standards and samples under a fume hood.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 To achieve the quantitation limits described in this method a minimum of 30 g of soil and 1 liter of liquid sample must be collected. More sample will be necessary if sample matrix spikes will be required.

8.2 Samples should be collected in cleaned glass containers with screw cap lids and Teflon liners. Plastic containers and/or plastic lined lids may NOT be used due to potential phthalate contamination.

8.3 Samples are stored at 4°C, and sample extracts are stored between -10 and -20°C and protected from light.

8.4 Analysis must be performed within 40 days of sample extraction.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Varian Gas chromatograph/mass spectrometer system

9.1.1 Varian Saturn II ion trap mass spectrometer is set up to scan from 40-450 mass units twice per second, using 70 volts (nominal) electron energy in the electron impact mode, and producing a mass spectrum that meets all the criteria in Table 3 when 5 ng of decafluorotriphenylphosphine (DFTPP) are injected onto the analytical column.

9.1.1.1 MS operating conditions:

- Electron energy: 70 volts (nominal).
- Mass range: 40-450 amu.
- Scan time: 820 amu/second = 2 scan/sec.
- Source temperature: 190°C
- Transfer line temperature: 250°C

9.1.1.2 GC operating conditions:

- Column Temperature Program: 45°C for 1.5 min, then to 200°C at 10°C/min, then to 315°C at 25°C/min, hold at 315°C until benzo[g,h,i]perylene has eluted
- SPI Injector Temperature Program: 45°C for 0.5 min, then to 300°C at 100°C/min
- Sample volume: 1 ul
- Carrier Gas: ultra high purity helium at 8psi (~2-3 ml/min)

9.1.2 Injector

9.1.2.1 A SPI (Septum Programmable Injector) temperature programmed injector that allows sub-ambient initial injector temperatures followed by rapid heating up to 315°C

9.1.3 Fused Silica Capillary Column: 30m x 0.32mm i.d. 1 um film thickness silicon coated DB-5MS or equivalent.

9.1.4 Data system: PC based multi-tasking computer that allows the continuous acquisition and storage on magnetic tape or compact disk of all mass spectra obtained throughout the duration of the chromatographic program. The software can search any GC/MS data file that was

acquired on the system for ions of a specific mass, and can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software allows integrating the abundances in any EICP between specified time or scan number limits. The 1992 version of the NIST mass spectral library is available for the identification of unknowns.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 When chromatography degrades or sensitivity decreases, routine maintenance consists of cleaning/changing injection port liner, clipping the capillary column, changing the injection port septa, and cleaning the ion trap.

11.0 CHEMICALS AND REAGENTS

11.1 All chemicals and reagents used must be pesticide grade or better, and must be determined to be free of interferences.

11.2 Acetone, Hexane, Methylene Chloride, Toluene - pesticide grade or equivalent.

12.0 STANDARDS PREPARATION

12.1 Stock quantitation standard solutions: Standard solutions are prepared from pure standard materials or purchased as certified solutions.

12.1.1 Commercially prepared stock standards are used to prepare the majority of quantitation working standards. They commonly come as mixes of compounds at 2000 mg/L sealed in various glass ampules that are combined during preparation. This mix is combined with the surrogate standard that is currently being used during sample extraction to create an 8270C quantitation standard. This standard is made up at a concentration of 200 mg/L using methylene chloride as the solvent. Dilutions of this 200 mg/L standard make up the 6 point initial calibration curve at concentrations of 25, 20, 15, 10, 5 and 2 mg/L. Benzoic acid and Benzidine responses are not linear in this concentration range, so extra stock standard of each of these is added. The range for Benzoic acid is 10-125 mg/L and 6-75 mg/L for Benzidine.

12.1.2 Lab made stock standard solutions from neat compounds are prepared by accurately weighing out the analyte to four significant figures. The material is dissolved in methylene chloride or other suitable solvent and diluted to volume in a volumetric flask. When compound purity is assayed to be 96% or greater, the weight is used without correction to calculate the concentration of the stock standard.

12.1.3 The stock standard solutions are transferred into screw-cap bottles with Teflon lined lids, stored at -10 to -20°C and protected from light. Stock standard solutions are monitored for signs of degradation or evaporation.

12.1.4 All stock standard mixes will be replaced annually or sooner if comparison with quality control check standards indicate a problem. Initial calibration curves and all dilutions of stocks except for the continuing calibration standards will be replaced every six months or sooner if comparison with quality control check standards indicate a problem. Continuing calibration standards will be re-diluted from stock weekly.

12.2 Internal standard solutions: The six internal standards used are 1,4-dichlorobenzene-d_4, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, naphthalene-d_8, and perylene-d_{12}. The stock standard is prepared at 1000 ng/uL by dissolving 100 mg of each compound with a small volume of methylene chloride and then diluting to 100 mL as described in 12.1.2. Each 1 mL sample extract undergoing analysis is spiked with 5 uL of the internal standard solution, resulting in a concentration of 5 ng/uL of each internal standard.

12.3 GC/MS tuning standard: The standard used to tune the mass spectrometer contains 5 ng/uL of decafluorotriphenylphosphine (DFTPP), and 50 ng/uL of pentachlorophenol, benzidine, and 4, 4' DDT, in methylene chloride. It is prepared as described in 12.1.2, and is used to tune the instrument, to verify injection port inertness, and to monitor GC column performance.

12.4 Surrogate standards: The surrogate standards used are o-terphenyl, 2-fluorophenol, phenol-d_6, 2,4,6-tribromophenol, nitrobenzene-d_5, and 2-fluorobiphenyl. These are prepared in methanol in the same manner as described in section 12.1.2. The base/neutral surrogate spike is made up at 200 mg/L and the acid surrogate spike is made up at 400 mg/L in methanol according to Method 3500. It is then combined for a base/neutral concentration of 100 mg/L and an acid concentration of 200 mg/L. The amount spiked is 100 uL per each one mL of final extract volume, resulting in a concentration of 10 ng/uL of base/neutral surrogates and 20 ng/uL acids per each mL of extract.

12.5 Matrix spike standards: The compounds in the base/neutral matrix spike solution are acenaphthene, 1,4-dichlorobenzene, 2,4,-dinitrotoluene, naphthalene, N-nitrosodi-n-propylamine, pyrene, and 1,2,4-trichlorobenzene. The acid spike contains 4-chloro-3-methyl phenol, 2-chlorophenol, 4-nitrophenol, pentachlorophenol, and phenol. Refer to section 12.1.2 for preparation techniques. The spikes are made up in methanol at concentrations of 100 mg/L for the base/neutral compounds and 200 mg/L for the acid compounds according to Method 3500. The standards are spiked in at 100 uL per each 1 mL of final extract volume resulting in a concentration of 10 ng/uL for the base/neutrals, and 20 ng/uL for the acids.

Note: For all State of Wisconsin samples, every analyte of interest must be spiked when preparing and analyzing matrix spikes and matrix spike duplicates. Spike amounts and concentrations will be the same as that specified above.

13.0 SAMPLE PREPARATION

13.1 For extraction procedures, see the appropriate Extraction Lab SOP, referenced in section 5.0.

13.2 All samples to be analyzed must be spiked with surrogates. See section 12.4 for specifics.

13.3 All samples are spiked with internal standard immediately prior to analysis. See section 12.4 for specifics.

13.4 Unknown or potentially highly contaminated extracts can be screened using a GC/FID with a 30m x 0.32mm i.d. DB-5 or equivalent capillary column with a 1 um film thickness. This minimizes contamination of the GC/MS system from unexpectedly high concentrations of organic compounds and/or matrix interferences.

14.0 CALIBRATION PROCEDURES

14.1 Set up instrument as specified in section 9.1.1.1 and 9.1.1.2.

14.2 All samples and standards are introduced into the system via direct injections. Manual injections are performed with a 10 uL syringe. Automated injections are performed using a Leap autosampler. 1 uL injections are performed on all samples and standards.

14.3 Each GC/MS system is hardware-tuned to meet the criteria in Table 3 for a 5 ng, 1 uL injection of DFTPP. No analyses may begin until these criteria are met. Spectra are taken across the apex of the 198 ion. Background subtraction is designed to only eliminate column bleed or instrument background ions. The GC/MS tuning standard is also used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Calculate the % breakdown as follows:

$$\%\ \text{deg radation} = \frac{\text{Area}_{DDE} + \text{Area}_{DDD}}{\text{Area}_{DDE} + \text{Area}_{DDD} + \text{Area}_{DDT}} \times 100$$

14.3.1 This result will be recorded on the daily instrument logbook.

14.3.2 Pentachlorophenol and benzidine should be present at their normal response, with minimal peak tailing. If peak tailing appears suspect, a tailing factor will be calculated on the total ion chromatogram of pentachlorophenol, following the instructions provided on Figure 1, to determine if corrective action is required. A tailing factor of 1 to 2 is considered acceptable, a tailing factor of 2 to 4 is considered to be the warning limit, and a tailing factor of 4 to 5 is considered unacceptable requiring corrective action. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to clip off the first 6-12 inches of the capillary column.

14.4 All analytes will be quantitated using the internal standard technique. Analytes and their corresponding internal standards are provided in Table 1 and 1A. For analytes not listed in either Table, the internal standard used for quantitation should be the one that elutes nearest the analyte. The ions used for quantitation are also provided in Table 1 and 1A. Only if interferences are noted can a secondary ion be used for quantitation. In this instance the RF for that compound must also be recalculated before any quantitation can take place.

14.5 Initial Calibration:

14.5.1 Calibration standards: A minimum of 5 points must be in the initial calibration curve. Table 1 calibration standards are typically run at levels of 2, 5, 10, 15, 20 and 25 ng/ul. The high, 25 ng/ul standard may be omitted; however, this is done at the expense of the linear range of the instrument. Each 1 mL aliquot of calibration standard is spiked with 5 uL of the internal standard solution prior to analysis. Other analytes, including those listed in Table 1A are run at appropriate concentrations based on the response of the analyte. The low point of the initial calibration curve must be at or below the required quantitation limit.

14.5.2 1 uL of each calibration standard (that also contains surrogates and internal standards) is analyzed. Figure 2 shows a chromatogram, with the proper chromatography, of a calibration standard containing the Method 8270C base/neutral and acid analytes. A Response Factor (RF) is calculated for each compound using the quantitation ion given in Table 1 or 1A, and the following formula:

$$RF = \frac{A_X \times C_{IS}}{A_{IS} \times C_X}$$

where:

A_X = Area of the characteristic ion for the compound being measured
A_{IS} = Area of the characteristic ion for the specific internal standard
C_X = Concentration of the compound being measured (ng/ul)
C_{IS} = Concentration of the specific internal standard (ng/ul)

14.5.3 A system performance check must be performed to ensure that average RFs are met before the calibration curve can be used. The System Performance Check Compounds (SPCCs) are listed in Table 4. The minimum acceptable average RF for the SPCC compounds is 0.050. The SPCC compounds typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated. The minimum RF for all non-SPCC compounds that are analytes of interest is ≥ 0.01.

14.5.4 The percent relative standard deviation is calculated for each compound using the following formula:

$$\%RSD = \frac{SD}{RF} \times 100$$

where:

SD = The standard deviation of the response factor for that analyte across the initial calibration curve.

RF = The average of the response factor for that analyte across the five point curve.

14.5.5 The percent RSD for each compound should be less than 15%. However, the percent RSD for each individual calibration check compound (CCC) MUST be less than 30%. If the percent RSD is **greater** than 30% for any CCC, corrective action, including replacing the injection port liner, replacing or clipping the capillary column, and recalibration of the GC/MS system, must be initiated.

14.5.6 The relative retention time of each compound of interest in each calibration run should agree within 0.06 relative retention time units.

14.5.7 If the percent RSD of any non-CCC compound is 15% or less, the relative response factor is assumed to be constant over the calibration range, and the average response factor should be used for quantitation.

14.5.8 If the percent RSD for any compound is greater than 15%, calibration curves should be constructed for those compounds by plotting the area ratio ($Area_{analyte}/Area_{IS}$) versus the concentration. A first order or higher regression fit should be used for the five calibration points. The analyst should select the regression order that gives the least amount of calibration error.

NOTE: It is not the intent of the method to allow non-linear calibration to be used to compensate for proper instrument maintenance. Thus, non-linear calibration must not be employed for methods or instruments previously shown to exhibit linear calibration for an analyte.

14.6 Continuing Calibration:

14.6.1 Prior to analysis of samples or standards, the DFTPP tuning standard is analyzed and evaluated as specified in section 14.3. These criteria must be demonstrated at the beginning of each 12-hr shift.

14.6.2 Immediately following every acceptable DFTPP analysis, continuing calibration standard(s) are run at a mid-level concentration. For the 8270C analytes listed in Table 1, the continuing calibration standard is run at 10 ng/ul. This standard contains all semi-volatile target analytes, including all required surrogates and internal standards. Other analytes, including those provided in Table 1A, are run at a continuing calibration standard concentration appropriate for the response of the compound. The response factors from the standards are compared with the average response factor from the initial calibration run on the same instrument.

14.6.3 System Performance Check Compounds (SPCCs): A system performance check is made on every continuing calibration standard. The SPCC criteria must be met in order for the continuing calibration standard to pass. The SPCC compounds listed in Table 4 are used for the continuing calibration run. The minimum RF for semi-volatile SPCCs is 0.050. The minimum RF for all non-SPCC compounds of interest is 0.01. If the minimum response

factors are not met, the system is evaluated, and corrective action is taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, or active sites in the column or chromatographic system. This check must always be met before analysis begins.

14.6.4 Calibration Check Compounds (CCCs): After the system performance check is met, the CCCs listed in Table 5 are used to check the validity of the initial calibration. Calculate the percent difference when using the average response factor model calibration:

$$\% \text{ Difference} = \frac{RF_v - RF_m}{RF_m} \times 100$$

where:

RF_v = response factor from verification standard
RF_m = average calibration factor from initial calibration

Use percent drift when calibrating using a regression fit model:

$$\% \text{ Drift} = \frac{C_1 - C_C}{C_1} \times 100$$

where:

C_1 = CCC Standard Concentration
C_C = measured concentration using appropriate quantitation method.

14.6.5 If the percent difference or drift for each CCC is less than ≤20%, the initial calibration is assumed to be valid. If any one CCC has a >20% difference from the initial calibration curve, corrective action must be taken. Problems similar to those listed under section 14.6.3 could also affect the CCC criteria. If the source of the problem cannot be determined after corrective action has taken place, the instrument is considered out of control. At a minimum the continuing calibration standard must be re-run. If necessary, a new curve will be run. The CCC criteria must also always be met before sample analysis begins.

NOTE: It is not the intent of the method to allow non-linear calibration to be used to compensate for proper instrument maintenance. Thus, non-linear calibration verification must not be employed for methods or instruments previously shown to exhibit linear initial calibration for an analyte.

14.6.6 The internal standard responses and retention times in the continuing calibration verification standard(s) and samples must be evaluated for each run. If the retention time for any internal standard varies by more than 30 seconds from the last calibration verification standard, the system must be inspected for malfunctions, and corrective action performed as necessary. If the EICP area for any of the internal standards varies by a factor of 2 (-50% to +100%) from

the midpoint standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrective action performed as necessary. All samples analyzed under either of these out of control conditions musts be re-analyzed.

15.0 ANALYTICAL PROCEDURE

15.1 Every 12 hour shift **must** begin with the analysis of DFTPP, followed by either a 5 point curve or a continuing calibration standard, and then a blank.

15.2 DFTPP **must** pass the required tuning criteria specified in section 14.3 before any subsequent analysis can begin. There is a 12 hour window that all acquisitions **must** be started in, beginning at the injection time of DFTPP. The entire 12 hour shift must be run under the same mass spectrometer conditions used for DFTPP. All samples must be run under the same gas chromatographic conditions as the quantitation standard. See 9.1.1.1 and 9.1.1.2 for recommended operating conditions.

15.3 Any compound requiring quantitation under Method 8270C **must** have an average Response Factor (RF) generated from a 5 point curve, and that curve **must** pass the required System Performance Check Compounds (SPCCs), and the Calibration Check Compounds (CCCs) specified in section 14.5.

15.4 A continuing calibration standard is run on days that a curve is not, and it also **must** pass the required criteria listed in section 14.6.

15.5 The analytical system **must** be demonstrated to be free from contamination under the conditions of the analysis by running a blank at least at the beginning of every 12 hour shift (see section 18.3).

15.6 A matrix spike, matrix spike duplicate, and laboratory fortified blank **must** be run for each quality control batch (up to a maximum of 20 samples/batch) to assess accuracy. Additional quality control method requirements are specified in the Quality Assurance section, 18.0.

16.0 CALCULATIONS AND DATA HANDLING

16.1 Qualitative analysis:

16.1.1 An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). These standard reference spectra are obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (a) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (b) correspondence of the sample component and the standard component mass spectrum.

16.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component in the daily continuing calibration standard. If co-elution of interfering components prohibits accurate assignment of the sample

component RRT from the total ion chromatogram, the RRT is assigned by using extracted ion current profiles for ions unique to the component of interest.

16.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%), are automatically checked by the software to be present in the sample spectrum. The relative intensities of ions must agree within plus or minus 30% between the standard and sample spectra. For example, an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.

16.1.2 For samples containing components not associated with the calibration standards, a library search can be made for the purpose of tentative identification. Only after visual comparison of sample spectra with the nearest library searches will the analyst assign a tentative identification. Guidelines for making tentative identification are:

16.1.2.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

16.1.2.2 The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

16.1.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

16.1.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

16.1.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

16.2 Quantitative analysis:

16.2.1 When a compound has been identified, quantitation of that compound is performed using the area of the quantitation ions listed in Tables 1 and 1A. Quantitation is performed using the internal standard technique. Internal standards are specified in Tables 1 and 1A. For targets not in either Table, the internal standard nearest the retention time of the analyte will be used. All qualitative results will be reported without correction for recovery data, and without subtraction of blank amounts.

16.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{Concentration in ug/L} = \frac{(A_x)(I_s)(V_t)(\text{Dil})}{(A_{is})(\text{RF})(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured
I_s = Amount of internal standard injected in ug/ml
V_t = Volume of total extract in ml
A_{is} = Area of characteristic ion for the internal standard
RF = Average response factor for compound being measured (section 14.5.2)
V_o = Volume of water extracted in liters
Dil = Any post extraction dilution factor

Sediment/Soil Sludge:

$$\text{Concentration in mg/kg} = \frac{(A_x)(I_s)(V_t)(\text{Dil})}{(A_{is})(\text{RF})(W_s)(D)}$$

where:

W_s = Weight of sample extracted in grams
D = % solids
all others same as for water

Note: If the compound detected has not met the 15 percent RSD requirement, the analyst must use the regression line fitted from the initial calibration to determine the extract concentration.

16.2.3 When requested, an estimate of concentration for non calibrated components in the sample is made. The formulas given above are used with the following modifications: The areas A_x and A_{is} are from the total ion chromatograms and the RF for the compound is assumed to be 1. The nearest internal standard free of interferences will be used. The concentration obtained is reported indicating that the value is estimated.

16.2.4 If the response for any quantitation ion exceeds the curve range of the initial calibration of the GC/MS system, a dilution of the extract is made. Dilute the sample only enough to bring the analytes in question into the upper half of the calibration curve. Additional internal standard is added to the diluted extract to maintain the required 5 ng/uL of each internal standard in the extracted volume. The diluted extract is then re-analyzed.

17.0 DATA REPORTING AND DELIVERABLES

17.1 The analyst running a set of samples is also responsible for correctly filling out, turning in, and filing the associated paperwork. It is essential to perform these tasks for the laboratory to be able to provide the client with defensible data.

17.2 LIMS Reporting

17.2.1 When the analyst has finished running a set of samples the data must be turned into the Laboratory Information Management System (LIMS). The benchsheets must be filled in completely to ensure that the results are reported correctly, and the data is associated with the right quality control batch. It is important that all required benchsheet information be filled in correctly and completely. This includes the quality control batch number from the extraction summary, the analytical batch information from the 12 hour shift, and the dilution factor. Dilution Factors are used to elevate the quantitation limits based on post extraction sample dilutions. The dilution factor may or may not equal the dilution ratio made.

17.2.2 Positive results must be recorded by crossing out the printed quantitation limit and recording the positive result on the right hand side. This is the result that has already been through all necessary calculations, including the dilution factor. If a positive result is detected in a diluted sample, the elevated quantitation limit must also be written on the left of the default quantitation limit.

17.2.3 Surrogate results are reported as amount found in the extract, amount spiked in the extract, and percent recoveries. Figure 3 provides an example of a completed analytical benchsheet.

17.2.4 If there are spikes, quality control benchsheets must also be completed and turned in. In addition to the requirements listed elsewhere in this section, quality control benchsheets also require the spiked amounts, percent recoveries, and percent differences where applicable. If out of control results are present due to extraction or severe matrix problems, the exclude (EXC) box must be checked to prevent the data from biasing the recovery window statistics. Figures 4-6 provide examples of quality control benchsheets.

17.2.5 An extracted Method Preparation Blank (MPB) benchsheet must be turned in for every extraction batch. A daily blank (BLK) must be turned in with every 12 hour shift. When the MPB is run, provided the MPB is clean, the MPB may also be the BLK. Turn in both sets of benchsheets. If running both 8270 and 625 samples, BLK, MPB, and Laboratory Fortified Blank (LFB) benchsheets must be turned in for each method. It is important to remember that a LFB cannot be turned in without also having turned in the associated MPB.

17.2.6 If internal chain-of-custody is required it is very important that the COC sheet is filled out correctly and returned to the COC file location.

17.2.7 All LIMS benchsheets (including the COC sheets) are placed in the correctly colored folders and turned into the data entry person responsible for entering the results. The blue folders containing the BLKs should also have the raw data quantitation reports and chromatograms included.

17.3 Laboratory Required Paperwork

17.3.1 All run, maintenance, tape, and standard logbooks must be filled in completely and correctly. Corrections are to be made with a lineout, not a writeover, and must be dated and initialized. Blank lines in the run logbook must be Z'd out. See Figure 7 and 8 for standard and run logbook examples.

17.3.2 All tune, curves and continuing calibration standard runs, and internal standard reports must be placed in their correct binders.

17.3.3 All LIMS documentation (except for the sample and quality control benchsheets), and the raw data (except for that specified above) must be placed in the correct folder and turned into the Semi-Volatile Laboratory technician. The technician will then record the date, time, and contents that were turned in. Sample and quality control benchsheets are returned to the proper folder after data review and approval.

17.4 CLP Like Deliverables

17.4.1 The following copies are required for all data packages that require CLP like deliverables:

- Copies of all tunes including the EICP that has the ion peaks for DFTPP, Benzidine, and Pentachlorophenol with the tailing factor calculations and results, and the ion abundance results and requirements.
- Copies of all associated curves, including the raw data quantitation reports, chromatograms, and Form VIs.
- Copies of all associated continuing calibration standards, including the raw data quantitation reports, chromatograms, and Form VIIs.
- Copies of all sample raw data quantitation reports, including triple plots for positive hits, chromatograms, and all associated TIC reports when requested. Quality control raw data, including blanks, are not necessary.
- Internal standard area count results and requirements for all samples.

17.5 Rounding and Significant Figures

17.5.1 Rounding is performed on the final quantitated result only. For all non-quality control results, results of < 10 ppb are rounded to 1 significant figure. Results ≥ 10 ppb are reported to 2 significant figures.

17.5.2 Quality control results are reported to 3 significant figures.

18.0 QUALITY ASSURANCE

18.1 Each laboratory that uses these methods is required to operate a formal quality control program. The program consist of the following requirements previously covered:

a) DFTPP (section 14.3)
b) Initial Calibration (section 14.5)
c) Continuing Calibration (section 14.6)

18.2 In addition to the above, the following quality control requirements must be followed.

18.3 Blank

18.3.1 After DFTPP and the curve or continuing calibration has been run, a blank is required before any samples are analyzed showing that the analytical system is free from interferences and contamination. This blank will be either a Method Preparation Blank (MPB) or a solvent Daily Blank (BLK). The MPB is the blank extracted with a set of samples, and the BLK is methylene chloride spiked with internal standard. The MPB will be run when available, and the BLK will be run when the extracted MPB has already been run. See section 17.2.3 for blank reporting requirements. At a minimum a blank is run at this point during every 12 hour shift. A blank will be run more frequently if contamination is suspected from a high level sample or if laboratory contamination is in question. MPBs must be spiked with surrogates and carried through the same stages of preparation as the samples.

18.4 Internal Standards

18.4.1 The internal standard responses and retention times in all runs following the continuing calibration standard must be evaluated immediately after or during data acquisition. The retention time for all internal standards must be within ± 30 seconds from the current 12 hour continuing calibration standard. The area of the quantitation ion for all internal standards must stay within a factor of two (-50% to +100%) from the current 12 hour continuing calibration standard.

18.4.2 Any time an internal standard fails the -50% to +100% area criteria, the ability to accurately quantitate an analyte is lost. For that reason every effort will be made to prevent the failure of an internal standard. Refer to the Corrective Action SOP for the procedure to follow when an internal standard fails. If many samples are out of control for no apparent reason, the mass spectrometer needs to be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning are necessary.

18.5 Surrogates

18.5.1 All samples must be spiked with surrogate standards. Until thirty samples of a given matrix have been analyzed, default recovery windows of 50-150% will be used. Once thirty samples of a given matrix have been analyzed, in house recovery windows will be generated (section 18.5.2-18.5.4) and used. Table 6 also provides examples of in house generated surrogate

recovery windows. These are examples only. At a minimum surrogate recovery limits will be updated annually on a matrix by matrix basis.

18.5.2 Calculate the upper and lower control limit for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

where

p = average percent recovery
s = standard deviation of the percent recovery

18.5.3 Two standard deviations will be used when 3 standard deviations give a negative lower control limit.

18.5.4 If recovery is not within limits, the Corrective Action SOP outlines if, or how the data is to be qualified. If many samples are out of control for no apparent reason, the mass spectrometer needs to be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning are required.

18.6 Matrix and Method Spikes

18.6.1 To assess accuracy, the laboratory must extract a Matrix Spike (SPK1), a Matrix Spike Duplicate (SPK2), and a Laboratory Fortified Blank (LFB), containing the compounds in Table 7, at least once every 20 samples extracted per matrix. If only one to ten samples are analyzed in a month, at least one matrix spike, one matrix spike duplicate, and one laboratory fortified blank is required. The LFB must be extracted daily. Generally the MPB and LFB are run at the beginning of the 12 hour shift, and the matrix spikes at the end. Running the matrix spikes at the end of the shift will help to document that the instrument was still operating correctly during the end of the 12 hour shift.

Note: For the State of Wisconsin samples, all routine 8270C analytes must be added for all spikes and spike duplicates.

18.6.2 Until 5 matrix spikes, matrix spike duplicates, and laboratory fortified blanks have been analyzed, the recoveries of the matrix spike, matrix spike duplicate, and laboratory fortified blank will be validated against default recovery windows of 50-150. Matrix Spike/Matrix Spike Duplicate precision limits will use a default precision limit of ± 20%.

18.6.3 Once five sets of the quality controls samples of a given matrix (waters, soils, etc.) have been analyzed, calculate the average percent recovery (R) and the standard deviation of the percent recovery (SD) per matrix. Express the accuracy assessment as a percent recovery interval from R - 3SD to R + 3SD. If, for example, R = 90 percent and SD = 10 percent, then the accuracy

interval is expressed as 60-120. Another set of limits will be calculated the same way for the laboratory fortified blank windows. Precision windows will be calculated by taking the average of the 5 percent differences ± 3 standard deviations. Windows will be updated at least annually.

18.6.4 Calculate the percent recovery as follows:

$$\%\ \text{recovery} = \frac{(A_{spk} - A_{smp})}{SPK} \times 100$$

where:

Aspk = actual concentration found in the spiked sample, in ug/L
Asmp = amount found in non-spiked sample, in ug/L

$$SPK = \left(\frac{\text{concentration of spiked standard in ug/L} \times \text{ml spiked}}{\text{initial sample volume in L}} \right)$$

18.6.5 Calculate the relative percent difference as follows:

$$\%RPD = \frac{(SPK1 - SPK2)}{\left[\frac{(SPK1 + SPK2)}{2}\right]} \times 100$$

where:

SPK1 = ug/L found in matrix spike
SPK2 = ug/L found in matrix spike duplicate

18.6.6 If recovery, or precision, is not within limits, the Corrective Action SOP will determine if, or how, the data is to be qualified:

18.6.7 If the LFB is out of control, the problem must be immediately identified and corrected before any further samples for that analyte can be run. The purpose of the LFB is to verify that out-of-control compounds in the MS or MSD are the result of matrix interferences rather than extraction or system errors. Failure of any part of an LFB will require some sort of corrective action, depending on the failed parameter. Every effort will be made to determine the reason for the failure (mis-spiked, mis-extracted, etc.) and appropriate actions will be taken. The Corrective Action SOP details how to proceed when a LFB fails

18.7 Method Detection Limit Studies

18.7.1 A Method Detection Limit (MDL) study must be performed for every analyte to be quantitated by method 8270C. MDL studies must be performed on all mass spectrometers involved in analysis of samples by this method. Results obtained for analytes for which an MDL has not

been calculated by this method must be considered estimated. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. Actual minimum quantitation limits are derived from the MDL study. MDL studies are run for both waters and soils. Minimum quantitation limits are equal to the amount spiked for the MDL study provided that the MDL passed. The quantitation limit actually achieved in any given analysis will vary depending on instrument sensitivity, matrix effects, and dilutions.

18.7.2 The procedure followed for a MDL study is based on the method given in the Federal Register, Part 136, Appendix B, latest revision. All Method 8270 quality control procedures governing the analyses must be followed.

18.7.3 Seven replicate analyses are performed using reagent water spiked with every analyte of interest, at the estimated minimum quantitation limit concentration.

18.7.4 If a blank measurement is required to calculate the measured level of an analyte, seven separate blanks must be run, one after each of the seven MDL samples. The average blank measurement is subtracted from all seven MDL runs.

18.7.5 The standard deviation of the amount found (blank-subtracted if necessary) for each analyte of the seven runs is calculated and multiplied by 3.143. The resulting number is the calculated MDL.

18.7.6 If the amount spiked is $\geq$ the calculated MDL and $\leq$ 5 times the calculated MDL, and there are no 0 percent recoveries in the set of seven, the MDL result is acceptable. If not the MDL must be re-run, only for the compounds that did not pass. If the study needs to be re-run at a different concentration, the entire set of seven needs to be re-run. If the study does not pass due to poor reproducibility on one of the samples, only that run needs to be re-analyzed. All seven runs do not need to be run in the 12 hour same shift.

18.7.7 If at any time the MDL Level is above a client's or state's desired quantitation limit, the "Calculated MDL" may be used for a quantitation limit if it the report is narrated. The narration needs to state that the quantitation limit is a "Calculated MDL" and when the particular compound is spiked at that level it is not observed.

18.7.8 The curve on the instrument being used to conduct the analysis must have as its low point the vial concentration of a sample spiked at the "MDL Level". A curve starting above this number can lead to large potential errors. For example: If the concentration of a sample spiked at the "MDL Level" of 0.10 ug/L is extracted as the MDL was extracted (i.e. 1000 mL to 1 ml, or 1000x concentration), the vial concentration will be 0.1 mg/L and this must also be the concentration of the low curve point. Consequently, assuming the MDL passed, 0.10 ug/L is the minimum quantitation limit reportable without narrating the results with the above mentioned qualifier.

18.7.9 Table 8 shows an example of a MDL spreadsheet used to calculate and verify MDLs and quantitation limits.

19.0 ANALYST CERTIFICATION/METHOD VALIDATION

19.1 Before the analysis of any actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running a one time analyst certification. While the analyst certification is not instrument dependent, this certification is required on every instrument that will be running samples to demonstrate instrument ability to generate acceptable accuracy and precision.

19.2 Prepare the certification samples at 100 ug/L by spiking 1 mL of a 100 ng/uL standard containing all the compounds of interest into 1 liter and extracting down to 10 ml. The spiking standard used must be prepared independently from the standard used for quantitation.

19.3 Analyze the four distilled check samples following the SOP. Calculate the average recovery (x) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

19.3.1 For each analyte x must be in the range of the current LIMS LFB limits and s must be less than or equal to 20. If s and x for all analytes meet the acceptance criteria, the analyst certification is acceptable. The analyst and the system are now permitted to run samples following this SOP. If any individual s exceeds the precision limit or any individual falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

19.3.2 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to 19.4.

19.4 Locate and correct the source of the problem and repeat the test for all analytes that failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all unacceptable compounds, beginning with section 19.1. Samples may not be analyzed by any analyst, or on any instrument, until the analyst certification has been successfully completed. Copies of the successful analyst certifications/method validations spreadsheet and raw data should be given to the Quality Assurance Manager.

20.0 REFERENCES

20.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition*, Final Update III, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry", Revision 3, December 1996.

20.2 *40 Code of Federal Regulations, most current edition*, Pt. 136, App. A, Method 625-Base/Neutrals and Acids.

20.3 *40 Code of Federal Regulations, most current edition*, Pt. 136, App. B, Definition and Procedure for the Determination of the Method Detection Limit.

21.0 ATTACHMENTS/APPENDICES

21.1 Table 1 – Targets, Retention Times, Quantitation & Secondary Ions

21.2 Table 1A – Additional Targets, Retention Times, Quantitation & Secondary Ions

21.3 Table 2 – Default Quantitation Limits

21.4 Table 2A – Default Quantitation Limits

21.5 Table 3 – DFTPP Key Ions and Ion Abundance Criteria

21.6 Table 4 – SPCC Criteria

21.7 Table 5 – CCC Criteria

21.8 Table 6 – Surrogates and Percent Recovery Windows

21.9 Table 7 – Spiking Compounds and Percent Recovery Windows

21.10 Table 8 – Method Detection Limit Study Example*

21.11 Table 9 – Analyst Certification Example*

21.12 Figure 1 – Tailing Factor of Pentachlorophenol

21.13 Figure 2 – 100 ppm Continuing Calibration Standard Total Ion Chromatogram

21.14 Figure 3 – Completed Analytical Benchsheet

21.15 Figure 4 – 6 Completed Quality Control Benchsheets

21.16 Figure 7 – Standard Logbook

21.17 Figure 8 – Analytical Run Logbook

*Only part of the Table or Benchsheet example has been included.

TABLE 1
TARGETS, RETENTION TIMES, QUANTITATION & SECONDARY IONS

Compound	Retention Time (min.)*	Quantitation Ion	Secondary Ion(s)	Internal Standard
Acenaphthene-d_{10} (I.S.)	17.76	162	162, 160	3
Chrysene-d_{12} (I.S.)	25.04	240	120, 236	5
Dichlorobenzene-1,4-d_4 (I.S.)	10.06	152	150, 115	1
Naphthalene-d_8 (I.S.)	13.21	136	68	2
Perylene-d_{12} (I.S.)	29.83	264+265	260, 265	6
Phenanthrene-d_{10} (I.S.)	20.50	188	94,80	4
2-Fluorobiphenyl (surr.)	16.00	172	171	3
2-Fluorophenol (surr.)	7.18	112	64	1
Nitrobenzene-d_5 (surr.)	11.38	127+128	128, 54	2
Phenol-d_6 (surr.)	9.13	99		1
2,4,6-Tribromophenol (surr.)	19.33	330	332, 141	3
Terphenyl-o (surr.)	21.03	230	215,229	5
Acenaphthene	17.84	152+154	153, 152	3
Acenaphthylene	17.44	152	151, 153	3
Anthracene	20.63	178	176, 179	4
Benzoic acid	12.39	105	77,122	2
Benzo(a)anthracene	25.00	228	229, 226	5
Benzo(b and k)fluoranthene	28.24/28.40	252	253, 125	6
Benzo(g,h,i)perylene	37.32	276+277	138, 277	6
Benzo(a)pyrene	29.60	252	253, 125	6
Benzyl alcohol	10.35	108	79, 77	1
Bis(2-chloroethoxy)methane	12.51	92+93	95, 123	2
Bis(2-chloroethyl)ether	9.38	92+93	63, 951	1
Bis(2-chloroisopropyl)ether	10.65	45	77, 121	1
Bis(2-ethylhexyl)phthalate	24.59	149	167, 279	5
4-Bromophenyl phenyl ether	19.73	248	250, 141	4
Butyl benzyl phthalate	23.56	149	91, 206	5
4-Chloroaniline	13.40	127	129	2
2-Chloronaphthalene	16.34	162	127, 164	3
4-Chloro-3-methylphenol	14.60	107	144, 142	2
2-Chlorophenol	9.57	128	64, 130	1
4-Chlorophenyl phenyl ether	18.87	204	206, 141	3

Approved By: 12/14/98 QA Manager

Approved By: 12/14/98 Area Manager

TABLE 1 (con't)
TARGETS, RETENTION TIMES, QUANTITATION & SECONDARY IONS

Compound	Retention Time (min.)*	Quantitation Ion	Secondary Ion(s)	Internal Standard
Chrysene	25.10	228	226, 229	5
Dibenz(a,h)anthracene	35.57	278	139, 279	6
Dibenzofuran	18.20	168	139	3
Di-n-butylphthalate	21.23	149	150, 104	4
1,3-Dichlorobenzene	9.93	146	148, 111	1
1,4-Dichlorobenzene	10.10	146	148, 111	1
1,2-Dichlorobenzene	10.45	146	148, 111	1
3,3'-Dichlorobenzidine	24.80	252	254, 126	5
2,4-Dichlorophenol	12.84	162	164, 98	2
Diethylphthalate	18.59	149+177	177, 150	3
2,4-Dimethylphenol	12.26	107	121, 122	2
Dimethylphthalate	17.03	163	194, 164	3
4,6-Dinitro-2-methylphenol	18.94	198	51, 105	4
2,4-Dinitrophenol	17.86	184	63, 154	3
2,4-Dinitrotoluene	18.12	165	63, 89	3
2,6-Dinitrotoluene	17.20	165	63, 89	3
1,2-Diphenylhydrazine	19.15	77	105, 182	4
Di-n-octylphthalate	26.32	149	167, 43	6
Fluoranthene	22.35	202	101, 203	4
Fluorene	18.89	166	165, 167	3
Hexachlorobenzene	19.87	284	142, 249	4
Hexachlorobutadiene	13.54	225	223, 227	2
Hexachlorocyclopentadiene	15.45	237	235, 272	3
Hexachloroethane	11.30	119	201, 199	1
Indeno(1,2,3-cd)pyrene	35.52	276+277	138, 227	6
Isophorone	12.00	82	95, 138	2
2-Methylnapthalene	15.06	142	141	2
2-Methylphenol (o-cresol)	10.58	108	79,107	1
3- and/or 4-Methylphenol (m,p-cresol)	10.95	108	79,107	1
Naphthalene	13.26	128	129, 127	2

Approved By: 12/14/98 QA Manager
Approved By: 12/14/98 Area Manager

TABLE 1 (con't)
TARGETS, RETENTION TIMES, QUANTITATION & SECONDARY IONS

Compound	Retention Time (min.)*	Quantitation Ion	Secondary Ion(s)	Internal Standard
2-Nitroaniline	16.59	138	92, 138	3
3-Nitroaniline	17.62	138	108, 92	3
4-Nitroaniline	18.90	108+138	108, 92	3
Nitrobenzene	11.43	77+123	65	2
2-Nitrophenol	12.21	109+139	109, 65	2
4-Nitrophenol	18.02	65	109, 65	3
N-Nitrosodimethylamine	4.58	73+74	42	1
N-Nitrosodiphenylamine	19.08	169	168, 167	4
N-Nitrosodipropylamine	10.95	70	42, 101, 1	1
Pentachlorophenol	20.18	266	264, 268	4
Phenanthrene	20.54	178	179, 176	4
Phenol	9.17	94	65, 66	1
Pyrene	22.74	202	200, 203	5
1,2,4-Trichlorobenzene	13.05	180	182, 145	2
2,4,5-Trichlorophenol	15.91	196	198, 200	3
2,4,6-Trichlorophenol	15.79	196	198, 200	3

I.S. = Internal Standard
surr. = Surrogate
* retention time provided for example only.

TABLE 1A
ADDITIONAL TARGETS, RETENTION TIMES, QUANTITATION & SECONDARY IONS

Compound	Retention Time (min.)*	Quantitation Ion	Secondary Ion(s)	Internal Standard
Acenaphthene-d_{10} (I.S.)	17.05	162	160,164	3
Chrysene-d_{12} (I.S.)	24.14	240	120,236	5
Dichlorobenzene-1,4-d_4 (I.S.)	9.39	152	150,115	1
Naphthalene-d_8 (I.S.)	12.49	136	68	2
Perylene-d_{12} (I.S.)	28.22	264+265	260	6
Phenanthrene-d_{10} (I.S.)	19.96	188	94,80	4
Acetophenone	10.45	105	77,70	2
2-Acetylaminofluorene	23.74	181	223,180	3
4-Aminobiphenyl	18.63	169	168,167	3
Aniline	8.76	93	66,65	1
Aramite**	22.64/22.73/22.85	185	63,57	4
2-sec-Butyl-4,6-dinitrophenol	19.89	211	163,147	3
2,6-Dichlorophenol	12.[illegible]	162	164,63	2
p-(Dimethylamino)azobenzene	22.71	120	225,77	3
7,12-Dimethylbenz(a)anthracene	26.79	256	252,241	5
3,3'-Dimethylbenzidine	23.26	212	213,106	3
2,2-Dimethylphenethylamine	12.64	58	91	2
1,3-Dinitrobenzene	16.55	167+168	139,169	2
Ethyl methacrylate	4.98	69	41,99	1
Ethyl methanesulfonate	7.74	79	109,97	1
Hexachlorophene	27.48	196	198,209	6
Hexachloropropene	12.75	213	215,211	2
Isosafrole	15.58	162	131,104	2
Methapyrilene	21.39	58	97,72	3
3-Methylcholanthrene	29.28	268	126,252	5
Methyl methacrylate	3.67	69	41,100	1
Methyl methanesulfonate	6.34	80	65,79	1
1,4-Naphthoquinone	16.23	158	104,102	2
1-Naphthylamine	17.87	143	115,116	2
2-Naphthylamine	18.05	143	115,116	2
4-Nitroquinoline-1-oxide	21.38	190	89,101	4

Approved By: [illegible] 12/14/98 QA Manager

Approved By: [illegible] 12/14/98 Area Manager

TABLE 1A (con't)
ADDITIONAL TARGETS, RETENTION TIMES, QUANTITATION & SECONDARY IONS

Compound	Retention Time (min.)*	Quantitation Ion	Secondary Ion(s)	Internal Standard
N-Nitroso-di-n-butylamine	13.64	84	57,41	2
N-Nitrosodiethylamine	7.14	102	42,44	1
N-Nitrosomethylethylamine	5.75	88	42,43	1
N-Nitrosomorpholine	10.48	56	116,86	2
N-Nitrosopiperidine	11.24	114	42,56	2
N-Nitrosopyrrolidine	10.39	100	41,42	1
5-Nitro-o-toluidine	18.42	152	106,77	3
Pentachlorobenzene	17.46	250	252,248	3
Pentachloroethane	8.74	167	93,117	2
Pentachloronitrobenzene	19.78	237	169,142	4
Phenacetin	19.17	108	109,179	3
p-Phenylenediamine	13.80	108	80,107	2
2-Picoline	6.73	93	66,92	1
Pronamide	20.20	173	175,145	3
Pyridine	6.32	79	52,51	1
Safrole	14.24	162	131,101	2
1,2,4,5-Tetrachlorobenzene	14.76	216	214,218	3
2,3,4,6-Tetrachlorophenol	17.83	232	230,234	3
o-Toluidine	10.54	107	106,79	2
sym-Trinitrobenzene	19.09	75	74,213	3
Octachlorocyclopentene (C-58)	19.03	307+309	237	3

I.S. = Internal Standard
* retention time provided for example only.
** Aramite chromatographs into three peaks

Approved By: 12/14/98 QA Manager
Approved By: 12/14/98 Area Manager

TABLE 2
DEFAULT QUANTITATION LIMITS

Semivolatiles	CAS Number	Default Quantitation Limits** Surface/ Ground Water ug/L	Low Soil/ Sediment mg/kg
Acenaphthene	83-32-9	5	0.33
Acenaphthylene	208-96-8	5	0.33
Anthracene	120-12-7	5	0.33
Benzoic acid	65-85-0	50	3.3
Benzo(a)anthracene	56-55-3	5	0.33
Benzo(b and k)fluoranthene	205-99-2 / 207-08-9	5	0.33
Benzo(g,h,i)perylene	191-24-2	5	0.33
Benzo(a)pyrene	50-32-8	5	0.33
Benzyl alcohol	100-51-6	50	1.3
Bis(2-chloroethoxy)methane	111-91-1	5	0.33
Bis(2-chloroethyl)ether	111-44-4	5	0.33
Bis(2-chloroisopropyl)ether	39638-32-9	5	0.33
Bis(2-ethylhexyl)phthalate	117-81-7	5	0.33
4-Bromophenyl phenyl ether	101-55-3	5	0.33
Butyl benzyl phthalate	85-68-7	5	0.33
4-Chloroaniline	106-47-8	20	1.3
2-Chloronaphthalene	91-58-7	5	0.33
4-Chloro-3-methylphenol	59-50-7	5	0.33
2-Chlorophenol	95-57-8	5	0.33
4-Chlorophenyl phenyl ether	7005-72-3	5	0.33
Chrysene	218-01-9	5	0.33
Dibenz(a,h)anthracene	53-70-3	5	0.33
Dibenzofuran	132-64-9	5	0.33
Di-n-butylphthalate	84-74-2	5	0.33
1,3-Dichlorobenzene	541-73-1	5	0.33
1,4-Dichlorobenzene	106-46-7	5	0.33
1,2-Dichlorobenzene	95-50-1	5	0.33
3,3'-Dichlorobenzidine	91-94-1	20	2.0
2,4-Dichlorophenol	120-83-2	5	0.33
Diethylphthalate	84-66-2	5	0.33

Approved By: 12/14/98 QA Manager
Approved By: 12/14/98 Area Manager

TABLE 2 (con't)
DEFAULT QUANTITATION LIMITS

Semivolatiles	CAS Number	Default Quantitation Limits** Surface/ Ground Water ug/L	Low Soil/ Sediment mg/kg
2,4-Dimethylphenol	105-67-9	5	0.33
Dimethylphthalate	131-11-3	5	0.33
4,6-Dinitro-2-methylphenol	534-52-1	20	1.7
2,4-Dinitrophenol	51-28-5	20	1.7
2,4-Dinitrotoluene	121-14-2	5	0.33
2,6-Dinitrotoluene	606-20-2	5	0.33
Diphenylamine	122-39-4	5	0.33
Di-n-octylphthalate	117-84-0	5	0.33
Fluoranthene	206-44-0	5	0.33
Fluorene	86-73-7	5	0.33
Hexachlorobenzene	118-74-1	5	0.33
Hexachlorobutadiene	87-68-3	5	0.33
Hexachlorocyclopentadiene	77-47-4	5	0.33
Hexachloroethane	67-72-1	5	0.33
Indeno(1,2,3-cd)pyrene	193-39-5	5	0.33
Isophorone	78-59-1	5	0.33
2-Methylnaphthalene	91-57-6	5	0.33
2-Methylphenol (o-cresol)	95-48-7	5	0.33
3- and/or 4-Methylphenol (m,p-cresol)	106-44-5	5	0.33
Naphthalene	91-20-3	5	0.33
2-Nitroaniline	88-74-4	20	1.7
3-Nitroaniline	99-09-2	20	1.7
4-Nitroaniline	100-01-6	20	1.7
Nitrobenzene	98-95-3	5	0.33
2-Nitrophenol	88-75-5	5	0.33
4-Nitrophenol	100-02-7	20	1.7
N-Nitrosodimethylamine	62-75-9	5	0.33
N-Nitrosodiphenylamine	86-30-6	5	0.33
N-Nitrosodipropylamine	621-64-7	5	0.33
Pentachlorophenol	87-86-5	20	1.7

Approved By: RL 12/14/98 QA Manager
Approved By: 12/14/98 Area Manager

TABLE 2 (con't)
DEFAULT QUANTITATION LIMITS

Semivolatiles	CAS Number	Default Quantitation Limits** Surface/ Ground Water ug/L	Low Soil/ Sediment mg/kg
Phenanthrene	85-01-8	5	0.33
Phenol	108-95-2	5	0.33
Pyrene	129-00-0	5	0.33
1,2,4-Trichlorobenzene	120-82-1	5	0.33
2,4,5-Trichlorophenol	95-95-4	5	0.33
2,4,6-Trichlorophenol	88-06-2	5	0.33

* Sample quantitation limits are highly matrix-dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

** Water quantitation limits are based on 1000 mL to 1 mL extracted MDL study. Quantitation limits listed for soil/sediment are based on an extraction of 30 g to 1 ml. The sample must be ≥ 50% solids.

TABLE 2A
ADDITIONAL DEFAULT QUANTITATION LIMITS

Semivolatiles	CAS Number	Default Quantitation Limits** Surface/ Ground Water ug/L	Low Soil/ Sediment mg/kg
Acetophenone	98-86-2	10	0.33
2-Acetylaminofluorene	53-96-3	50	2.0
4-Aminobiphenyl	92-67-1	10	0.33
Aniline	62-53-3	5	1.7
Aramite	140-57-8	50	2.0
2-sec-Butyl-4,6-dinitrophenol	88-85-7	5	2.0
2,6-Dichlorophenol	87-65-0	5	0.33
p-(Dimethylamino)azobenzene	60-11-7	10	0.33
7,12-Dimethylbenz(a)anthracene	57-97-6	10	0.33
3,3'-Dimethylbenzidine	119-93-7	50	2.0
2,2-Dimethylphenethylamine	122-09-8	20	0.70
1,3-Dinitrobenzene	99-65-0	5	0.33
Ethyl methacrylate	97-63-2	50	2.0
Ethyl methanesulfonate	62-50-0	10	1.0
Hexachlorophene	70-30-4	***	***
Hexachloropropene	1888-71-7	50	2.0
Isosafrole	120-58-1	20	0.70
Methapyrilene	91-80-5	10	1.0
3-Methylcholanthrene	56-49-5	50	2.0
Methyl methacrylate	80-62-6	50	2.0
Methyl methanesulfonate	66-27-3	50	2.0
1,4-Naphthoquinone	130-15-4	1000	30
1-Naphthylamine	134-32-7	50	2.0
2-Naphthylamine	91-59-8	50	2.0
4-Nitroquinoline-1-oxide	56-57-5	500	20
N-Nitroso-di-n-butylamine	924-16-3	20	0.90
N-Nitrosodiethylamine	55-18-5	5	2.0
N-Nitrosomethylethylamine	62-75-9	5	2.0
N-Nitrosomorpholine	59-89-2	20	0.70
N-Nitrosopiperidine	100-75-4	20	0.70

Approved By: 12/14/98 QA Manager Approved By: 12/14/98 Area Manager

TABLE 3
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-80% of mass 198
68	<2% of mass 69
69	Present
70	<2% of mass 69
127	25-75% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance (see note)
199	5-9% of mass 198
275	10-30% of mass 198
365	>0.75% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	15-24% of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110% that of m/z 198.

TABLE 4
SYSTEM PERFORMANCE CHECK COMPOUNDS (SPCCs)

Base/Neutral Fraction	Acid Fraction
N-nitroso-di-n-propylamine	2,4-Dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

TABLE 5
CALIBRATION CHECK COMPOUNDS (CCCs)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

Approved By: RL 12/14/98 **QA Manager** **Approved By:** JO 12/14/98 **Area Manager**

TABLE 2A (con't)
ADDITIONAL DEFAULT QUANTITATION LIMITS

Semivolatiles	CAS Number	Default Quantitation Limits** Surface/ Ground Water ug/L	Low Soil/ Sediment mg/kg
N-Nitrosopyrrolidine	930-55-2	20	0.70
5-Nitro-o-toluidine	99-55-8	10	0.33
Pentachlorobenzene	608-93-5	5	0.33
Pentachloroethane	76-01-7	50	2.0
Pentachloronitrobenzene	82-68-8	20	0.50
Phenacetin	62-44-2	10	0.33
p-Phenylenediamine	106-50-3	***	***
2-Picoline	109-06-8	20	0.70
Pronamide	23950-58-5	10	0.33
Pyridine	110-86-1	10	0.33
Safrole	94-59-7	10	0.33
1,2,4,5-Tetrachlorobenzene	95-94-3	10	0.50
2,3,4,6-Tetrachlorophenol	58-90-2	50	2.0
o-Toluidine	95-53-4	10	0.33
sym-Trinitrobenzene	99-35-4	20	0.70
Octachlorocyclopentene (C-58)	706-78-5	0.1	0.02

* Sample quantitation limits are highly matrix-dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

** Water quantitation limits are based on 1000 mL to 1 mL extracted MDL study. Quantitation limits listed for soil/sediment are based on an extraction of 30 g to 1 ml. The sample must be ≥ 50% solids.

*** These compounds have been demonstrated to be difficult to extract from water, or difficult to chromatograph. Detection limits are not available.

Approved By: 12/14/98 QA Manager

Approved By: 12/14/98 Area Manager

TABLE 6
EXAMPLE* OF SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Calculated % Recoveries Water	Calculated % Recoveries Soil
Nitrobeuzene-d_5	34-120	15-132
2-Fluorobiphenyl	39-118	30-124
o-Terphenyl	29-133	26-128
Phenol-d_6	2-46	12-133
2-Fluorophenol	6-69	3-129
2,4,6-Tribromophenol	28-130	5-132

* This Table is provided as an example only. Actual windows are updated periodically and may be different at the time samples are run.