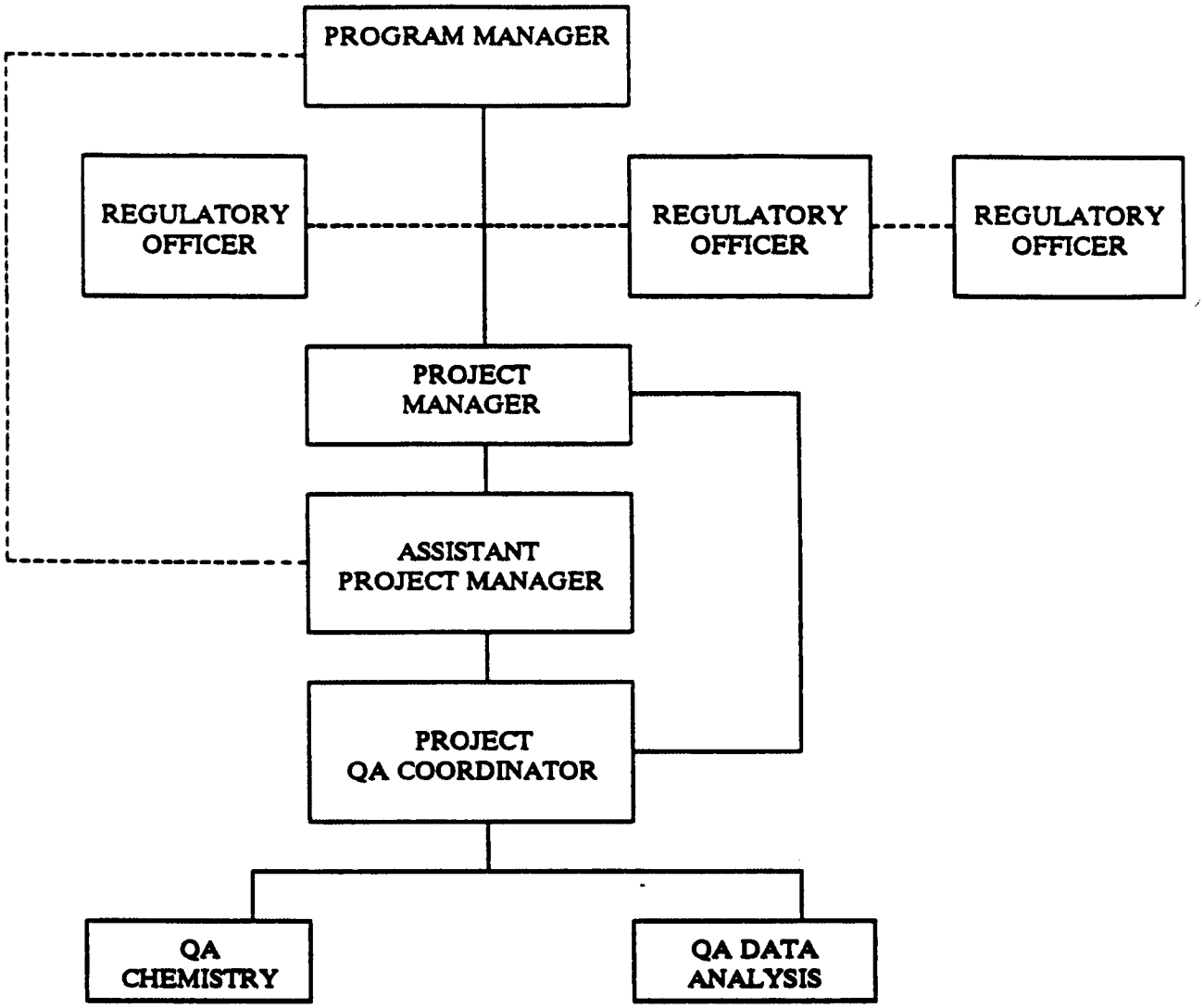
APPENDIX A

Example QA/QC Checklists, Forms, and Records

CONTENTS

QA PROGRAM ORGANIZATION FLOW DIAGRAM



EXAMPLE DATA QUALITY OBJECTIVES FOR ACCURACY AND COMPLETENESS

Variable	Matrix	Units	Target Detection Limit	Bias (%)	Precision (%)	Completeness (%)	Method	Reference	Maximum Holding Time
Volatiles	Sediment	µg/kg	10	±50%	±30%	99%	Purge & Trap/GC-MS	EPA abc/x-cc-yy(1975)	14 days
Grain Size	Sediment	Percent	0.01	—	±5%	99%	Sieve & Pipet		Undetermined

ALTERATION CHECKLIST

Sample Program Identification: _____

Material to be Sampled: _____

Measurement Parameter: _____

Standard Procedure for Analysis: _____

_____

Reference: _____

_____

_____

Variation from Standard Procedure: _____

_____

_____

Reason for Variation: _____

_____

_____

Resultant Change in Field Sampling Procedure: _____

_____

_____

Special Equipment, Material, or Personnel Required: _____

_____

_____

Author's Name: _____ Date: _____

Approval: _____ Title: _____

Date: _____

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
SAMPLERS: *(Signature)*	

STA. NO.	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	ANALYSIS						REMARKS

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

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

FIELD TRACKING REPORT FORM

W/O No. _____ Page _____

FIELD TRACKING REPORT: _____-_____
(LOC-SN)

FIELD SAMPLE CODE (FSC)	BRIEF DESCRIPTION	DATE	TIME	SAMPLER

LABORATORY TRACKING REPORT FORM

W/O No. _____ Page _____

LABORATORY TRACKING REPORT: _____-_____
(LOC-SN)

FRACTION CODE	X	PREP/ANAL REQUIRED	RESPONSIBLE INDIVIDUAL	DATE DELIVERED	DATE COMPLETED

GENERAL SAMPLE LABEL

(NAME OF SAMPLING ORGANIZATION)

PROJECT: _____

DATE: _____

TIME: _____

SAMPLE ID NO.: _____

MEDIA: _____

STATION NUMBER: _____

DEPTH: _____

PRESERVATION: _____

ANALYSES TO BE PERFORMED: _____

SAMPLED BY: _____

LAB NO.: _____

REMARKS: _____

STATION LOCATION LOG

DATE: _____

PROJECT: _____

STATION LOCATION: _____

DESCRIPTION OF SAMPLES COLLECTED: _____

SPC ZONE: _____(N/S) EAST: _____ NORTH: _____

_____

LOCATION:

Bottom Depth: _____ (ft) _____ (m) Tide: ± _____ (m) MLLW: _____ (ft) _____ (m)

LORAN C: LOP1 _____ LOP2 _____

Variable Radar Range: _____

_____

_____

Visual Fixes: (Note: Please tape any drawings to back of this sheet)

_____

_____

_____

Photos - Roll: _____ Pictures: _____

PID Reading (range): _____

Comments: _____

_____

_____

RECORDER: _____ SIGNATURE: _____ ORG. CORE _____ DATE: _____

SYSTEMS AUDIT CHECKLIST

SAMPLE PROGRAM IDENTIFICATION: _____

SAMPLING DATES: _____

MATERIAL TO BE SAMPLED: _____

MEASUREMENT PARAMETER: _____

SAMPLING AND MONITORING EQUIPMENT IN USE:

_____

_____

_____

_____

AUDIT PROCEDURES AND FREQUENCY: _____

_____

_____

_____

FIELD CALIBRATION PROCEDURES AND FREQUENCY: _____

_____

_____

SIGNATURE OF QA COORDINATOR: _____

DATE: _____

CORRECTIVE ACTIONS CHECKLIST

SAMPLE PROGRAM IDENTIFICATION: _____

SAMPLING DATES: _____

MATERIAL TO BE SAMPLED: _____

MEASUREMENT PARAMETER: _____

ACCEPTABLE DATA RANGE:

_____

CORRECTIVE ACTIONS INITIATED BY: _____

TITLE: _____

DATE: _____

PROBLEM AREAS REQUIRING CORRECTIVE ACTION: _____

_____

_____

_____

MEASURES TO CORRECT PROBLEMS: _____

_____

_____

MEANS OF DETECTING PROBLEMS (FIELD OBSERVATIONS, SYSTEMS AUDIT, ETC): _____

_____

_____

APPROVAL FOR CORRECTIVE ACTIONS: _____

TITLE: _____

SIGNATURE: _____

DATE: _____

APPENDIX B

Example Statement of Work for the Laboratory

PREFACE

This appendix contains a generic statement of work for the analysis of most chemicals in the most commonly analyzed sample matrices.

CONTENTS

STATEMENT OF WORK

The following tasks shall be performed by _____ as extensions to work identified as part of Contract No. ____ between Contractor and _____.

SUMMARY OF ANALYSES AND SERVICES

The Laboratory shall perform quantitative analyses for the analytes listed in Table 1 on sediment, water, and tissue samples collected from in and around _____. The analyses shall be conducted according to _____ sampling and analysis plan (SAP), the project work plan, and _____.

SAMPLE DELIVERY AND STORAGE

Sampling will begin approximately _____, and continue for a period of approximately _____. Contractor will provide samples to the Laboratory no earlier than _____. Table 2 summarizes the maximum number of samples the Laboratory could receive each month and the associated analyses. The actual number of samples that will be delivered to the Laboratory may vary from these estimates.

Samples will be sent from the site to the Laboratory's facilities via United Parcel Service or equivalent carrier. Contractor may choose to use the Laboratory's courier service if the Laboratory provides such a service. Contractor will coordinate with the Laboratory for final disposition of the samples after analysis. All samples shall be maintained under strict chain of custody at all times, including documentation of any transfers among facilities.

METHODS

The Laboratory shall perform the analyses according to the specified _____, or other Contractor-specified protocols. Table 1 provides a list of specific method references, holding times, and data quality objectives.

The Laboratory shall promptly notify the Contractor Quality Assurance and Quality Control (QA/QC) Coordinator prior to any deviation from these methods. Further, the Laboratory shall immediately notify the Contractor QA/QC Coordinator as soon as it becomes apparent that the data quality objectives cannot be met for a set of samples.

TABLE B-1. SUMMARY OF ANALYSES AND DATA QUALITY OBJECTIVES

Analyte	Matrix	Units	Target Detection Limit	Bias (%)	Precision (%)	Completeness (%)	Method Reference	Holding Time (days)
Organic Analyses								
TCL[a] semivolatile organic compounds	Solids Water Tissue	µg/kg µg/L µg/kg						
TCL volatile organic compounds	Solids Water Tissue	µg/kg µg/L µg/kg						
TCL pesticides and PCBs[b]	Solids Water Tissue	µg/kg µg/L µg/kg						
Lipids	Tissue	µg/kg						
Metals Analyses								
Copper	Solids Water	µg/kg µg/L						
Mercury	Solids Water Tissue	µg/kg µg/L µg/kg						
TAL[c] metals	Solids Water Tissue	µg/kg µg/L µg/kg						
Conventional and Nutrient-Related Analyses								
Acid-volatile sulfide	Solids	µmoles/g						
Total organic carbon	Solids Water	% carbon mg/L						
Dissolved organic carbon	Water	mg/L						

TABLE B-1. (cont.)

Analyte	Matrix	Units	Target Detection Limit	Bias (%)	Precision (%)	Completeness (%)	Method Reference	Holding Time (days)
Physical Analyses								
Grain size	Solids	g dry wt.						
Percent moisture	Solids	% moisture						
Total suspended solids	Water	mg/L						

[a] Target compound list.
[b] Polychlorinated biphenyl.
[c] Target analyte list.

TABLE B-2. ESTIMATED MAXIMUM NUMBER OF SAMPLES BY MONTH AND ANALYTE TYPE

Analyte	(date) Maximum			(date) Maximum			(date) Maximum			(date) Maximum			Total Maximum		
	Solids	Water	Tissue	Solids	Water	Tissue	Solids	Water	Tissue	Solids	Water	Tissue	Solids	Water	Tissue
Organic Analyses															
TCL[a] semivolatile organic compounds															
TCL volatile organic compounds															
TCL pesticides and PCBs[b]															
Lipids															
Metals Analyses															
Copper															
Mercury															
TAL[c] metals															
Conventional and Nutrient-Related Analyses															
Acid-volatile sulfide															
Total inorganic carbon															
Dissolved organic carbon															
Physical Analyses															
Grain size															
Percent moisture															
Total suspended solids															

[a] Target compound list.
[b] Polychlorinated biphenyl.
[c] Target analyte list.

QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

The Laboratory shall implement the following procedures to assess quality during sample analysis:

- **Calibration Verification**—Initial calibration of instruments shall be performed at the start of the project and when any ongoing calibration does not meet control criteria. The number of points used in the initial calibration is defined in each analytical method (e.g., Contract Laboratory Program [CLP]). Ongoing calibration verification shall be performed as specified in the analytical methods to monitor instrument performance. In the event that an ongoing calibration is out of control, analysis of project samples shall be suspended until the source of the control failure is either eliminated or reduced to within control specifications. Any project samples analyzed while the instrument was out of control shall be reanalyzed at Laboratory's expense.

- **Surrogate Spike Compounds**—The Laboratory shall spike all project samples to be analyzed for organic compounds with appropriate surrogate compounds as defined in the analytical methods (e.g., CLP). Recoveries determined using these surrogate compounds shall be reported by the Laboratory; however, the Laboratory shall not correct sample results using these recoveries.

- **Method Blanks**—The Laboratory shall not apply blank corrections to original data. For organic analyses, a minimum of 1 method blank shall be analyzed for every extraction batch, or 1 for every 20 samples, whichever is more frequent. For metals and conventional analyses, 1 method blank shall be analyzed for every digestion batch, or 1 for every 20 samples, whichever is more frequent.

- **Matrix Spike Samples**—For organic analyses and metals, the Laboratory shall analyze a minimum of 1 matrix spike for each group of samples extracted or digested, or 1 for every 20 samples, whichever is more frequent. For organic analyses, 1 matrix spike duplicate shall either be analyzed for each group of samples extracted or for every 20 samples, whichever is more frequent.

- **Laboratory Control Samples**—When available, the Laboratory shall use laboratory control samples (LCS). For metals and applicable conventional parameters, 1 LCS shall either be analyzed for every digestion batch or for every 20 samples, whichever is more frequent. The source of the LCS must be included in the data package.

- **Laboratory Duplicates**—The Laboratory shall perform duplicate analyses as indicators of laboratory precision. For metals analyses (except mercury) and conventional analyses, the Laboratory shall analyze 1 laboratory duplicate either for every digestion batch or for every 20 samples, whichever is more frequent.

- **Sample Container Preparation**—Sample containers shall be prepared by the Laboratory and delivered to the project site, as required. Sampling personnel shall discard any containers that have visible signs of dirt or contamination. Documentation of the preparation of sample containers shall be prepared, signed, and dated by Laboratory personnel and included with the sample container shipment.

DELIVERABLES

The Laboratory shall report results that are supported by sufficient backup data and quality assurance results to enable reviewers to conclusively determine the quality of the data. The data and supporting documents shall be provided to the Contractor QA/QC Coordinator. The Laboratory shall not divulge outside of Contractor any data or other information obtained or generated by the Laboratory with respect to the work specified herein. Data reporting requirements are summarized below.

Laboratory Data Reports

All data reports shall include the following:

A. General

1. A cover letter documenting all sample preparation and analytical protocols used and explaining any variance from protocols contained in the appropriate EPA statement of work (SOW) or this SOW.

2. Copies of completed chain-of-custody records and sample analysis request forms.

3. A cross-referenced table of Contractor and Laboratory identification numbers, and full explanation of all data qualifier symbols in accordance with the appropriate EPA SOW.

4. Tabulated results in units specified in the appropriate EPA SOW or this SOW.

5. A table of sample preparation data, including initial weights or volumes of samples, final dilution volumes, and digestion or preparation reagents. Data must be grouped by preparation date and include the identity of all quality control checks associated with each preparation batch. If subsets of a large number of samples are prepared or digested at separate times, then each sample subset is defined as a batch. Data provided in this table must be sufficient to unequivocally match each field sample with the corresponding quality control check samples.

B. Quality Control Results

1. For the analyses of inorganic compounds, the following summary results should be tabulated in the format of the appropriate indicated EPA form:

   a. Initial and ongoing calibration verifications

   b. Initial and ongoing calibration blanks and preparation blanks

   c. Inductively coupled plasma-atomic emission spectrometry (ICP) interference checks

   d. Matrix spike sample recoveries

   e. Duplicate samples

   f. Laboratory control sample recoveries

   g. Method of standard additions, if performed

   h. ICP serial dilution

   i. Mercury holding times, if performed

   j. Instrument detection limits

   k. ICP interelemental correction factors

   l. ICP linear ranges.

2. For all other analyses, the following tabulated summaries of all quality control checks for each analyte should be included:

   a. Initial and ongoing calibration verifications

   b. Initial and ongoing calibration blanks and preparation blanks

   c. Matrix spike sample recoveries

   d. Duplicate samples

   e. Independent standards.

C. Original Data

1. Legible photocopies of all original data, including Laboratory notebook pages, computer printouts, and stripcharts, with sufficient information to unequivocally identify the following:

   a. Calibration and ongoing calibration results

   b. Surrogate spike compound recoveries

c. Samples and all dilutions

d. Results of all method blanks

e. Results of all matrix spikes and matrix spike duplicates

f. Results and origin of LCS analyses

g. Results of Laboratory duplicates and triplicates

h. Origin of all reference materials

i. Any instrument adjustments or apparent anomalies on the measurement record.

2. The following information should be shown on the first page of each set of original data sheets pertaining to a particular protocol (e.g., ICP computer printout):

   a. A statement documenting the analyte(s) and the exact protocol used

   b. The date of analysis

   c. Typed name and signature of the analyst.

3. Copies of all sample container preparation documentation.

D. Electronic Deliverables

All data reported on the EPA forms must also be submitted as a diskette deliverable. The data should be in Format A (on an MS-DOS diskette), as defined by the SOW.

E. Other Information

Although not required as a deliverable for every data package, the following documentation must be available at the request of the Contractor QA/QC Coordinator as part of the Laboratory's standard QA/QC procedures:

- All original data
- Sample receipt and storage logbooks
- Record of sample holding time
- Storage temperature logbooks
- Conductivity of distilled/deionized water
- Analytical balance annual and routine (Class S weights) calibration logbooks

- Standard preparation and tracking logbooks, including purity of chemicals used to prepare standards
- Instrument calibration protocols and service record logbooks, including preventive maintenance
- Evidence of spot-checking of data handling
- In-house quality control charts.

TURNAROUND TIME

Schedules for delivery of results may vary, but shall not exceed a turnaround time of __ calendar days. Generally, a turnaround time of __ days will be desired. For data that are delivered late, the Laboratory will be subject to, at the discretion of the Contractor, a penalty of __ percent per calendar day for each day the data are late up to a maximum of __ percent of the total cost of the analyses.

PROGRESS REPORTS, PROBLEM NOTIFICATION, AND PROJECT AUDITS

A verbal progress report to the Contractor QA/QC Coordinator is required each week for the duration of the project. Immediate notification of the Contractor QA/QC Coordinator is required when the Laboratory identifies a problem that could prevent all QA/QC requirements or data quality objectives, including required detection limits, to be met for the final data. Contractor may conduct onsite audits of the Laboratory's facilities during the period of analysis to assess implementation of QA/QC requirements. The Laboratory shall maintain records to support an audit of the technical quality of all analyses and shall provide all such records to Contractor upon request.

APPENDIX C

Description of Calibration, Quality Control Checks, and Widely Used Analytical Methods

CONTENTS

DESCRIPTION OF CALIBRATION, QUALITY CONTROL SAMPLES, AND WIDELY USED ANALYTICAL METHODS

INTRODUCTION

The relative importance, rationale, and recommended frequency of calibration and each of the quality control samples are discussed in the following sections. A summary of the major considerations in applying these procedures is provided in the main text (see Section 2.7).

The concepts of calibration and quality control samples apply to dozens of analytical methods that are currently used by laboratory technicians. Selection of appropriate methods for particular types of analyses is based on the list of chemicals for analysis and the required detection limits. Some of the widely used analytical methods are described below, along with technical issues that should be considered when choosing individual methods.

CALIBRATION

Calibration of analytical instruments is a critical element of quality control because the procedures used for calibration will determine both the accuracy and precision of analytical results. Gas chromatography/mass spectrometry, or any other analytical technique, measures the magnitude of an unknown concentration of an analyte relative to a known concentration of the analyte or a similar analyte in a standard. Such relative measurements are meaningless unless the responsiveness of the analytical instrument can be determined over a range of analyte concentrations. Through calibration, this level of responsiveness can be determined. The relationship between response and concentration is generally expressed as an analytical curve. For the analysis of organic compounds in samples, response factors (RFs) for analytes relative to standards at various concentrations may be established from this analytical curve. The degree with which incremental concentrations of an analyte produce constant increments of response is called *linearity*.

Guidelines for instrument calibration must be included in the statement of work for the laboratory performing the analysis. Examples of these guidelines are given in *Methods for Chemical Analysis of Water and Wastes* (U.S. EPA 1983). Project managers should ensure that the statement of work addresses the following points:

- Instruments should be calibrated at the beginning of the project before any samples are analyzed, after each major disruption in analytical procedures, and whenever action limits are exceeded for certain samples. This type of calibration is called the *initial calibration* of the instrument. Through initial calibration, an analytical curve based on the absorbance, emission intensity, or other measured characteristics of known standards can be established. Data from subsequent analyses are considered valid as long as the values fall within the linear range of this curve.

- In some analytical programs, the accuracy of the initial calibration is verified and documented for every analyte by analyzing U.S. Environmental Protection Agency (EPA) quality control solutions immediately following the initial calibration. If immediate verification is not required, then the verification may be conducted after several samples have been analyzed. When a certified solution of an analyte is not available from EPA or any other source, analyses should be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. When measurements for the certified components exceed the action limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the recalibration verified.

- The validity of the original calibration curve should be confirmed throughout the analyses of samples. This process is called *continuing calibration.* However, unless required by a specific method, the continuing calibration results should not be used to quantify sample results (use the average response from the initial calibration instead). For gas chromatography/mass spectrometry (GC/MS) analyses of samples containing organic compounds, calibration should be checked at the beginning of each work shift, at least once every 12 hours (or every 10–12 analyses, whichever is more frequent), and after the last sample analysis of each work shift. For gas chromatography/electron capture detection analyses, calibration should be checked at the beginning of each shift, every 6 hours (or every 6 samples, whichever is less frequent), and after the last sample analysis of each shift.

- For analyses with inductively coupled argon plasma emission spectrometry and atomic absorption spectrometry, all work should be performed using continuing calibration. A procedure for conducting these calibrations is outlined in EPA's Contract Laboratory Program statement of work for inorganic chemicals (U.S. EPA 1990e). Frequency of continuing calibration of these instruments is 10 percent of the samples or every 2 hours during an analysis run, whichever is more frequent.

QUALITY CONTROL SAMPLES

Blanks

Blanks are quality control samples that are processed with the samples but contain only reagents. They are used to obtain the response of an analysis in the absence of a sample, including assessment of contamination from sources external to the sample. Contamination can arise from sources such as the reagents themselves, sample or reagent containers, and equipment used for sampling, sample storage, and analysis. The types of analytical blanks used to identify each of these potential sources of contamination are described below:

- **Method blanks** (also called preparation blanks or reagent blanks) are used to identify any contamination that may have been contributed by laboratories during sample preparation. A method blank should be required for each batch of samples prepared for analysis, except in the case of volatile organic analyses (VOAs), in which case, method blanks should be analyzed at least once every 12 hours. Because method blanks are usually included in the cost of sample analysis, they should not place an additional cost burden on a project.

- **Bottle blanks** are used to determine whether sample containers are sources of contamination. One bottle blank should be prepared for each lot of sample containers. Large increases in the contaminant level for the bottle blank compared with the method blank indicate a potential container problem. Laboratories usually provide clean containers for performing bottle blank analyses at no additional cost. For most sampling efforts, precleaned containers from a chemical supply company can be obtained at reasonable cost. The use of precleaned bottles may eliminate the need to have bottle blanks analyzed.

- **Transport blanks** (also called trip blanks) are used to detect contamination arising during sample shipping, handling, and storage. These blanks are taken from clean containers filled with deionized water, transported to the field, and stored and shipped with the samples. One transport blank should be included with each shipping container. A contaminant level for the transport blank that greatly exceeds the contaminant level of the method blank indicates a potential field handling, container, or storage problem. Transport blanks are important only for projects involving analysis of volatile organic compounds, which may migrate from one container to another.

- **Field equipment blanks** (also called decontamination checks) are used to detect contamination arising from field sampling equipment. At least one field equipment blank should be required for each medium that is sampled during a sampling effort.

Matrix Spikes

Matrix spike samples are used to provide an indication of the bias due to matrix effects and an estimation of the precision of results. They can also provide indications of how tightly an analyte is bound to its matrix, such as soil or tissue. Matrix spike samples are created by adding known amounts of chemicals of interest to actual samples, prior to extraction and usually prior to digestion. The addition of these chemicals is commonly called spiking. The matrix spike is analyzed using the same analytical procedure used for samples. The results are then compared with the results from the analysis of a replicate, unspiked sample. In this way the effect of the particular sample matrix on the recovery of chemicals of concern can be evaluated. By spiking and analyzing the sample after digestion, an analyst can determine whether spike analysis results have been affected by matrix binding or by sample preparation procedures. This postdigestion spiking is only used for metals analyses.

Matrix spike samples should include a wide range of chemical types. For example, a matrix spike sample for analysis of semivolatile organic compounds may include spiking with three neutral compounds, two organic acid compounds, and two organic base compounds. Ideally, samples should be spiked either at approximately 5 times the expected chemical concentration in a sample or at 5 times the target detection limit, whichever is higher. Spiking at this concentration reduces the possibility for any increase in random error during the matrix spike analysis and eliminates any masking of interferences at representative chemical concentrations.

One matrix spike sample and one matrix spike duplicate sample should be analyzed for every set of twenty or fewer samples or with each sample preparation lot. If 20 or more samples are submitted, 1 matrix spike duplicate pair should be run for each set of 20 samples. Analysis of matrix spikes and matrix spike duplicates is often performed to assess the precision and bias of one set of results.

Surrogate Spikes

Surrogate spike compounds can be used to estimate the recovery of organic compounds in a sample. Surrogates are compounds with characteristics similar to those of compounds of interest that are added to a sample before it undergoes the process of extraction. Surrogates should be compounds that are not expected to be present in the samples, but they should have characteristics similar to the compounds of concern. Compounds labeled with stable isotopes (that is, where normal carbon or hydrogen atoms in the molecule have been replaced with isotopes of carbon or hydrogen) are commonly used as surrogates. However, all surrogates need not be isotopically labeled. They need only be compounds that are physically and chemically similar to the chemicals of interest. For example, dibromooctafluorobiphenyl is used by some laboratories as a surrogate for polychlorinated biphenyls (PCBs), although this compound is not identical in structure to a PCB.

Because surrogate compounds are the only means of checking method performance on a sample by sample basis, they should be used whenever possible. A minimum of five surrogate spikes (three neutral and two acid compounds) should be added to each sample when analyzing for semivolatile organic compounds. These surrogate spikes should cover a wide range of compound classes. At least three surrogate compounds should be used for the analysis of volatile organic compounds, and at least one surrogate compound should be used in each extracted sample as a check on recovery of pesticides. A separate surrogate compound should be used in each extracted sample to check the recovery of PCB mixtures.

Check Standards

Check standards contain known amounts of analyte and are analyzed along with the samples. Check standard results are used to indicate bias due to sample preparation and/or calibration and to control precision.

Laboratory Control Samples

Laboratory control samples are check standards used to assess precision in the analytical procedures for metals. Like reference materials, these samples can be acquired from EPA. Often they are routinely analyzed by the laboratory at no extra cost.

Spiked Method Blanks

In certain organic methods, surrogate spikes are added to the check standards; these quality control samples are called spiked method blanks. The different compounds and their required amounts are specified in EPA's guidelines for the Contract Laboratory Program (U.S. EPA 1990d,e) and other regional guidelines. Such analyses are useful to verify acceptable method performance prior to and during routine analysis of samples containing organic compounds. Spiked method blanks do not take into account sample matrix effects, but can be used to identify basic problems in procedural steps. Spiked method blanks can also be used to provide minimum recovery data when no suitable reference material is available or when sample size is insufficient for matrix spikes. A spiked method blank should be analyzed whenever a method is used for the first time in a project and each time that a method is modified. In these instances, analysis of the spiked method blank should take place before analysis of any samples.

Reference Materials

Reference materials are substances with well-characterized properties that are useful for assessing the bias of an analysis and auditing analytical performances among laboratories. SRMs are certified reference materials containing precise concentrations of chemicals,

accurately determined by a variety of technically valid procedures, and are issued by the National Institute of Standards and Technology. Currently, SRMs are not available for the physical measurements or all pollutants in sediments; however, where possible, available SRMs or other regional reference materials that have been repeatedly tested should be analyzed with every 20 samples processed. Further information on SRMs is provided in the main text (see Section 2.11.2).

Replicates

Replicates are two or more identical samples that are analyzed to provide an estimate of the overall precision of sampling or analytical procedures. When two separate samples are taken from the same field station, or when one sample is split into two separate samples, these replicate samples are specifically called *duplicates*. Duplicates are usually sufficient when using an analytical procedure that is well proven in the laboratory. Analyzing three replicate samples (called *triplicates*) yields more meaningful statistical measures of variability than analyzing duplicate samples. However, statistically combining the variance of duplicate sample results across several sets of duplicates is also an effective way of evaluating variability.

Replicate samples are commonly used for the following purposes:

- **Analytical (or laboratory) replicates** measure the precision of sample analyses. To prepare analytical replicates, the sample is homogenized by the laboratory and divided into two subsamples. The subsamples are then independently analyzed. If five or fewer samples are submitted for analysis, a minimum of one analytical replicate is recommended, the exact number to be determined by the project manager. If more than 5 but less than 20 samples are submitted, at least 1 analytical replicate should be analyzed. A general rule is 1 analytical replicate for every batch of up to 20 samples analyzed together (e.g., U.S. EPA 1990d).

- **Field replicates** measure sampling variability. These samples are collected at the same time and location as other samples and are submitted for analysis along with the other samples. Field replicates should be coordinated with analysis of laboratory replicates so that both sampling variability and analytical variability can be measured for the same station. The project manager or coordinator usually determines the frequency with which field replicates are collected and sent to the laboratory. If funds are limited, a single laboratory replicate to measure analytical variability is preferred over a field replicate.

- **Blind replicates** are samples submitted to the laboratory without the laboratory's prior knowledge. Data from these blind replicates can be used to detect potential laboratory bias when compared with data from the analysis of analytical replicates. In this manner, blind replicates can serve

as laboratory quality control samples. However, the results for these samples are subject to errors introduced by the process of splitting the sample and by preservation, transportation, and storage procedures as well as analytical errors. Analysis of 1 set of blind replicates should be performed whenever 20 or more samples are submitted. At least one triplicate set is recommended for analysis of more than 20 samples.

COMMON ANALYTICAL METHODS

Gas Chromatography

Gas chromatography is a technique used to separate a complex mixture of organic materials into its components (for example, an extract of oil or smoke, which may contain hundreds, even thousands, of compounds). To do this, the sample extract is injected into a heated chamber, in which the mixture of compounds is concentrated at the head of a separating column. The mixture is then carried through the column by an inert gas (called the *mobile phase*). As the column is heated, the analytes pass through absorbent materials (called the *stationary phase*). Different analytes move at different rates and appear one after another, along with any interfering substances for a particular analyte, at the effluent end of the column. Here they are measured by a *detector*. The detector sends information as an electronic signal to an integrator, chart recorder, or computer. The signals are then interpreted and presented graphically in the form of a *chromatogram* and digitally as a *quantification report*.

Using the chromatogram and the digital information contained in the quantification report, many analytes contained in the sample can be accurately identified and quantified. Several different gas chromatograph/detector combinations are commonly used for the analysis of volatile and semivolatile organic compounds, which include pesticides and PCBs. Three of these combinations are described in the following sections.

Gas Chromatography/Mass Spectrometry

GC/MS enables positive identification of a compound that has eluted from a gas chromatographic column. In the GC/MS chamber, separated compounds are bombarded by electrons and broken into characteristic fragments called *ions*. The mass of the charged ions (i.e., their molecular weight) can be sensed by a detector that accumulates data on ionization current over a wide range of masses. The more ions of a particular mass, the greater the ionization current that is recorded for that mass. At any one time, the relative intensity of this current over all the different masses recorded for a particular compound gives rise to its mass spectrum (Figure C-1). The pattern of fragmentation ions in a mass spectrum is used to distinguish one compound from another. In addition, the intensity of the current recorded for one characteristic ion over time gives rise to its mass chromatogram, which is used to quantify the concentration of the analyte as it

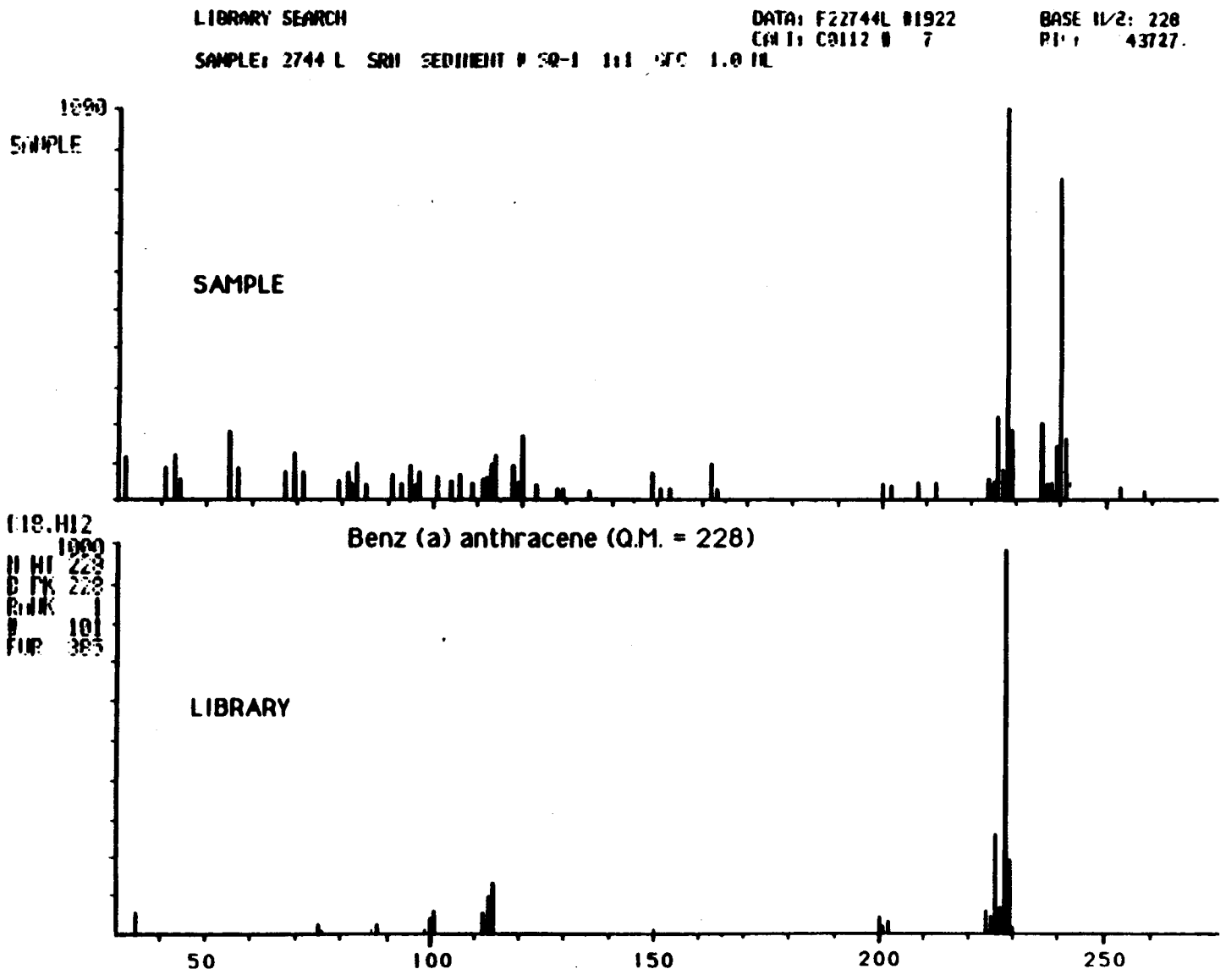


Figure C-1. Example mass spectrum for benz(a)anthracene identified in a sample sediment extract (upper) and authentic spectrum stored in computerized GC/MS library (lower).

elutes from the gas chromatograph. This characteristic ion is called the *quantification ion*. The mass chromatograms for all ions detected can be superimposed into a reconstructed ion chromatogram (RIC), also called a total ion chromatogram. The RIC is a graphic display of the total ionization current resulting from all mass fragments for all compounds detected from the start to the finish of the analysis. The RIC can be compared with the chromatograms produced by other detectors and provides an indication of the relative composition of components in the sample mixture analyzed by GC/MS. The mass spectrometer is a selective detector that allows for the positive identification of many compounds. Other kinds of detectors may be more sensitive in detecting PCBs and other chlorinated compounds.

Gas Chromatography/Electron Capture Detection

Gas chromatography/electron capture detection (GC/ECD) is useful for detecting analytes such as pesticides, PCBs, and other similarly structured chemical compounds that contain chlorine. The ECD measures the total concentration of a chemical in a sample, but it cannot distinguish one individual chemical from others. Verification of individual chemicals is accomplished by comparing the order in which the chemicals appear (called the *elution order*) and the time that passed before they appeared (called the *retention time*) with the elution orders and retention times of certain analytical standards. The identity of a chemical is verified when the elution orders and retention times match on two columns of different stationary phases. This verification technique, called *dual dissimilar column confirmation*, is useful because two chemicals that may have the same elution orders and retention times on one column will have different characteristics on the second column.

Gas Chromatography/Flame Ionization Detection

Gas chromatography/flame ionization detection (GC/FID) can be used to detect organic compounds that can be converted to ions during exposure to flame. This kind of detector is especially sensitive to molecules that contain carbon and hydrogen, just as the GC/ECD is especially sensitive to molecules containing chlorine. Because the GC/FID, like the GC/ECD, cannot distinguish between individual chemicals, dual dissimilar column confirmation must also be performed for each sample analyzed. Related detectors that use flame for analyzing organic samples include the nitrogen flame ionization detector (NFID), which is especially sensitive to nitrogen- and phosphorus-containing molecules, and the flame photometric detector (FPD), which is especially sensitive to organophosphorus pesticides and other compounds containing sulfur.

PACKED VS. CAPILLARY COLUMNS

Different kinds of separating columns will yield different results. Packed columns have been used routinely in the past for the analysis of PCBs, pesticides, and volatile organic compounds. Packed columns produce chromatograms of fairly low resolution, although the results may be reproducible (i.e., precise). However, a large quantity of the sample extract can be analyzed without overloading the instrument. More exacting analysis is afforded by either megabore capillary or fused silica capillary columns. Pesticides and PCBs can now be routinely analyzed using megabore columns. Analysis of volatile organic compounds can be conducted on capillary columns. However, because the entire sample purge is used for volatile analyses, a packed column with high loading capacity may still be preferred if high resolution is not essential. If project results are dependent on detailed recognition of contaminant mixtures (as is the case with PCBs and toxaphene), laboratories equipped with capillary columns should be selected to perform analytical tasks.

High Pressure Liquid Chromatography

Like gas chromatography, high pressure liquid chromatography (HPLC) is a technique used to separate a complex mixture into its component compounds. The compounds are carried as a liquid through solid absorbent phases and are sensed at the effluent end of the column by a specialized detector sensitive to, for example, ultraviolet, fluorescent, or infrared signals. This technique (described in EPA's laboratory manual *Test Methods for Evaluating Solid Waste* [U.S. EPA 1986a) is useful for analyzing polycyclic aromatic hydrocarbon (PAH) compounds in samples because many interferents on other instruments do not emit ultraviolet or fluorescent spectra, thereby increasing the sensitivity of the ultraviolet/fluorescent detector to many PAH compounds. However, some compounds of interest also do not emit these characteristic spectra. It is for this reason that EPA's Contract Laboratory Program statement of work for organic analysis recommends GC/MS over HPLC using ultraviolet/fluorescent detectors. However, HPLC can be useful as a way to screen samples for PAH contamination. Because it removes some interferents and separates the sample into components that can be individually collected and analyzed, HPLC can also be used as a powerful cleanup technique.

Atomic Absorption Spectrometry

Two basic methods of spectrometry are commonly used to identify and measure concentrations of metals in a sample. Using the first method, atomic absorption spectrometry, the digested sample is first vaporized and then exposed to a light source emitting a spectrum characteristic of the target analyte. A portion of the light is absorbed by the analyte in the sample. The remaining light is measured by a photoelectric detector and assigned a numerical value. Because the intensity of light absorbed by the sample is proportional to the quantity of the target analyte present in the light's path,

this value represents the concentration of a metal in the sample. Several different forms of atomic absorption are frequently used:

- Graphite furnace atomic absorption spectrometry (GFAA) determinations are completed as single element analyses. With this technique, sample digestates are vaporized in an electrically heated graphite furnace. The furnace is designed to gradually heat the digestates in several stages, allowing an experienced analyst to remove unwanted matrix components and select the optimum final temperature for the metal being analyzed. The major advantage of this technique is that it affords extremely low detection limits, which are particularly essential in the analysis of arsenic, cadmium, selenium, or lead. Samples must be relatively clean for GFAA to produce usable data.

- Hydride generation atomic absorption (HGAA) spectrometry uses a chemical reaction to separate arsenic or selenium selectively from a sample digestate. This technique removes these two elements from the sample matrix, minimizing interferences and improving instrument sensitivity.

- Cold vapor atomic absorption (CVAA) spectrometry uses a chemical reaction to release mercury from the digestate as a vapor, which is then analyzed by atomic absorption. This method should be used whenever analysis of mercury in samples is required.

- Flame atomic absorption (FLAA) spectrometry determinations are normally completed as single element analyses, following exposure of the vaporized samples to either a nitrous oxide/acetylene or air/acetylene flame. Data produced using this technique are relatively free of interferents, however instrument sensitivity is not as great as with other forms of atomic absorption.

Inductively Coupled Plasma-Atomic Emission Spectrometry

The second widely used and cost-effective form of spectrometry is inductively coupled plasma-atomic emission spectrometry (ICP). Using ICP, the digested sample is first turned into an aerosol, then subjected to extremely high temperatures within the instrument. The high temperature ionizes the atoms, which produce ionic emission spectra uniquely characteristic of specific metals. The wavelengths of these spectra can then be used to identify one or many different metals in the sample, while the intensity of light can be used to determine metals concentrations.

The primary advantage of ICP is that it allows simultaneous or rapid sequential determination of many different metals, reducing the time and cost of individual metals analyses. The primary disadvantage of ICP, however, is its lower degree of sensitivity. The detection limit associated with ICP analysis is often higher than the detection limit that can be obtained through the use of a graphite furnace or several other forms of atomic

absorption spectrometry. Although all ICP instruments use high-resolution optics and background corrections to minimize interferences, analysis for traces of metals in the presence of a large excess of a single metal can be difficult. Spectrometric data are reliable only if the analyte concentrations in the digestate are 5–10 times greater than the instrument detection limit. When concentrations are lower than this value for ICP analysis (as is often the case, for example, with samples containing arsenic or lead), then GFAA should be used. A relatively new method of detection is the use of combined inductively coupled plasma-mass spectrometry (ICP/MS), which not only allows for simultaneous determination of many different metals, but can also achieve lower detection limits comparable to those using graphite furnace techniques.

APPENDIX D

Example Standard Operating Procedures

CONTENTS

General Standard Operating Procedures

STANDARD OPERATING PROCEDURE
SAMPLE PACKAGING AND SHIPPING

For samples collected during field operations that will be classified as "environmental." Specific sample packaging and shipping requirements are described below.

ENVIRONMENTAL SAMPLES

All samples identified as Environmental Samples should be packaged and/or shipped utilizing the following procedures.

Packaging

1. Place samples into a strong container, such as a lined cooler or a U.S. Department of Transportation (DOT)-approved fiberboard box. The inside of the container should be lined with a polyethylene bag. Wrap glass jars with bubble-pack and surround the samples with noncombustible, absorbent, cushioning material for stability during transport.

2. Seal the large polyethylene bag with two chain-of-custody seals.

3. Place the laboratory/sampling (including chain-of-custody) paperwork in a large envelope and tape it to the inside lid of the shipping container (see Shipping Papers).

4. Close and seal the outside container with several chain-of-custody seals. Tape it shut using fiberglass tape.

Marking/Labeling

1. Use abbreviations only where specified.

2. Place the following information, either hand-printed or in label form, on the outside container:

   - Laboratory name and address
   - Return name and address.

3. Print "Environmental Samples" and "This End Up" clearly on top of the shipping container. Put upward pointing arrows on all four sides of the container. No other marking or labeling is required.

Shipping Papers

No DOT shipping papers are required. The following sample custody and analytical laboratory request forms should accompany the sample shipment. These documents should be taped to the inside lid of the outside sample container:

- Chain-of-custody form
- Sample analytical request form
- Sample packing list.

See the quality assurance project plan for procedures in filling out these forms.

STANDARD OPERATING PROCEDURE

EQUIPMENT DECONTAMINATION

The purpose of this standard operating procedure (SOP) is to define decontamination procedures for field equipment used for collecting soil, sediment, and water samples. Techniques for ridding equipment of both metals and organic contaminants are discussed. Sampling equipment is decontaminated between each sampling event to avoid cross contamination of samples and to help maintain a healthy working environment. Protective clothing is worn by all field technicians during sampling and decontamination as described in the health and safety plan.

It is the responsibility of the field sampling coordinator to assure that proper decontamination procedures are followed and that all waste materials produced by decontamination are properly managed. It is the responsibility of the project safety officer to draft and enforce safety measures that provide the best protection for all persons involved directly with sampling or decontamination. All subcontractors (e.g., drilling contractors) are required to follow the decontamination procedures specified in the contract, the health and safety plan, and this SOP. Individuals involved in sampling and/or decontamination are responsible for maintaining a clean working environment and ensuring that contaminants are not introduced to the environment.

All equipment will be decontaminated using a series of washes and rinses designed to remove materials of interest without leaving residues that will in any way interfere with analysis of the samples taken with that equipment. In addition, the decontamination site will be set up at a location separate from the sampling area in order to isolate these two activities.

Field equipment blanks will be taken at a frequency of 5 percent of samples and sent to the laboratory(s) for analysis along with the regular samples. These blanks will serve as a quality assurance indicator of possible cross contamination of samples. When feasible, samples to be taken with the same equipment will be taken in order from lowest to highest suspected contaminant levels to minimize the chances of cross contamination.

The following is a list of materials that are required on site to support decontamination. The quantity and actual use of each item will be dependent on the overall size and nature of the sampling effort.

- Cleaning liquids and dispensers: soap and/or phosphate free detergent solutions, tap water, methanol, 10 percent nitric acid, distilled/deionized water
- Personal safety gear as defined in the project health and safety plan
- Chemical-free paper towels and/or tissues
- Powder-free disposable latex gloves
- Waste storage containers: drums, boxes, plastic bags
- Plastic ground cloth on which to lay clean equipment
- Cleaning containers: plastic and/or galvanized steel tubs and buckets
- Cleaning brushes with non-contaminating stiff bristles
- Steam cleaning apparatus (supplied by drilling contractor).

The materials used in decontamination activities are located a minimum of 15–30 feet downwind of the sampling site as designated by the task leader. Decontamination will be carried out before moving to the next sampling site to avoid transporting contaminants.

PROCEDURES

Regardless of the type of contamination that requires removal, the basic steps involved are the same. Procedures unique to organic, metal, and organic/metal combined contamination are discussed in their respective sections that follow.

Step 1: Gross Removal of Material

Steam Cleaning

Depending on the availability of apparatus (e.g., drilling operations), steam cleaning combined with brushing is the preferred method of initial material removal. Using steam alone introduces little further contamination, and is a very efficient way of removing materials. Equipment such as spatulas, split spoons, and drill flights are placed in and/or suspended over tubs that catch contaminated wash waters for proper disposal.

Detergent Wash

In cases where steam apparatus is not available, a phosphate free detergent wash and tap water rinse may be used. A detergent bath is formulated in a tub large enough to hold the equipment to be washed leaving enough volume to hold the tap water rinses. All material is brushed from the equipment into the tub. The equipment is rinsed with tap water while suspended over the wash tub. Because detergents can contain low levels of interfering contaminants for both organic and metals analysis, the thoroughness of the final rinse in this step is of utmost importance. When the analyte levels in the samples to be taken by the decontaminated equipment are suspected to be very low (e.g., background level), it is recommended that the detergent wash be replaced by a distilled water wash or steam cleaning when available, followed by a decontamination equipment blank as described below.

Step 2: Specific Contaminant Removal

Organic Contaminants

For removal of general organic contaminants, the solvent of choice is methanol because a) it dissolves all contaminants of concern and b) it is miscible with water which means it can be removed with a water rinse. The equipment is suspended over a tub and rinsed from the top down with high purity methanol delivered by peristaltic pump for large pieces, or a squirt bottle for smaller pieces. Rinse wastes are disposed of according to the project health and safety plan.

Metal Contaminants

Metals require acid solvents for efficient removal. Nitric acid is the acid of choice because of its ability to dissolve all of the metals of concern. The equipment is suspended over a tub and rinsed from the top down with 10 percent nitric acid delivered by peristaltic pump for large pieces, or a squirt bottle for smaller pieces. Rinse wastes are disposed of according to the project health and safety plan.

Combined Organic/Metals Contaminants

When equipment will be used to take samples that will be analyzed for both metal and organic constituents, the acid rinse is performed followed by the methanol rinse, each as described above. Due to the difficulty in obtaining organics free acids, and the ease of obtaining metals free methanol, the order of the two rinses must not be reversed.

Step 3: Final Distilled/Deionized Water Rinse

A final rinse with distilled/deionized water is carried out last to remove the contaminant specific solvents (i.e., nitric acid and/or methanol). Because these solvents may themselves interfere with sample analyses, this step is very important and must be carried out thoroughly. The equipment is suspended over a waste tub, and rinsed from the top down with distilled/deionized water delivered by pump or squirt bottle, depending on equipment size. In the case of metals decontamination, a simple pH monitoring technique (e.g., pH paper) may be used to monitor rinse water in determining rinse completion.

Step 4: Air Dry

Before an equipment blank is taken, the equipment is laid out on a clean plastic ground cloth and allowed to dry. The equipment should be protected from gross contamination during the drying process.

Equipment Blanks

Equipment blanks are taken between selected samplings as described in the Sampling and Analysis Plan. Equipment is rinsed with distilled water that is subsequently collected in a sample container. The rinsate sample is then labeled and shipped as a blind sample to the laboratory(s) with regular samples. One blank is created in this way for each analysis to be performed on samples taken with this equipment unless otherwise stated in the quality assurance plan. The equipment should be protected from contamination between the time the blank is taken and the time the next sample is collected.

Specific Analytical Standard Operating Procedures

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR COLUMN CHROMATOGRAPHY OF SEMIVOLATILE ORGANIC ANALYTES IN SEDIMENT AND TISSUE EXTRACTS (REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard operating procedure for the preparation of columns for the cleanup and chemical class separation of semi-volatile organic compounds from marine samples. The extract fractions will be analyzed by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).

2.0 MATERIALS AND EQUIPMENT

9.5-mm ID X 45-cm glass chromatography column with 200 ml reservoir

Apparatus for determining weight
- Top-loading balance capable of weighing to 0.01 g

Turbo-Vap (Zymark) apparatus, with heated water bath maintained at 25-35° C
- Glass Turbo-Vap flasks, 200 ml
- Nitrogen gas, compressed, 99.9% pure

Tumbler, ball-mill

Glass graduated cylinders, 100- and 500-ml

Glass beakers, 50-ml

Borosilicate glass vials with Teflon-lined screw caps, 2-ml

Micropipets, solvent rinsed or muffled at 400°C

Reagents
- Pentane, pesticide grade or equivalent
- Methylene Chloride (CH_2Cl_2), pesticide grade or equivalent
- Hexane, pesticide grade or equivalent
- Heptane, pesticide grade or equivalent
- Deionized water, pentane-extracted

BioSil A silicic acid, 100-200 mesh
Glass wool, silanized

3.0 METHODS

3.1 Silica gel preparation

3.1.1 Approximately 150 grams of fully activated silica gel is accurately weighed and transferred to a glass jar.

3.1.2 The silica gel is deactivated by adding 7.5% (weight basis) of pentane-extracted deionized water. The water is weighed accurately and an appropriate amount is added dropwise, ~ 1 ml at a time, to the silica gel. After each water addition, the jar is hand-shaken vigorously.

3.1.3 The glass jar is then placed on a ball-mill tumbler and allowed to tumble overnight.

3.1.4 After tumbling, the jar is removed from the tumbler. The silica gel is stored tightly sealed in the jar at room temperature until use.

3.2 Column preparation

3.2.1 The glass columns are set up in ring stands in a fume hood.

3.2.2 Glass wool, sufficient to create a 1 cm thick plug in the column is placed into the reservoir of the column. A glass rod is used to push the glass wool to the bottom of the column.

3.2.3 11.5 g of the 7.5% deactivated silica gel is weighed out in a beaker. Approximately 30 ml of CH_2Cl_2 is added to the beaker to form a slurry. The slurry is then carefully poured into the column. The beaker is rinsed with additional CH_2Cl_2, as are the inner walls of the reservoir to ensure all silica is introduced to the column. The total volume of CH_2Cl_2 should be approximately 50 ml.

3.2.4 The column is allowed to drip, and the eluate is collected and discarded. When the level of the CH_2Cl_2 just reaches the top of the silica gel, 50 ml of pentane is slowly added to the column. This eluate is also collected and discarded.

3.3 Chemical class separations

3.3.1 The sample extract is introduced to the column just as the pentane rinse

level reaches the silica gel. The vial is then rinsed with an additional 1 ml of pentane which is also introduced to the column just before the silica gel is exposed. The eluate is collected in a clean round bottom flask.

3.3.2 As the sample rinse level reaches the silica gel, 55 ml of pentane is added to the column. The eluate is collected as the F-1 fraction in a clean Turbo-Vap flask.

3.3.3 As the pentane level reaches the top of the silica, 36 ml of 70:30 pentane:methylene chloride is introduced to the column. The F-2 fraction is collected in a separate Turbo-Vap flask from the F-1 fraction. After collection, the flasks are kept tightly capped with aluminum foil. At no time should the column flow rate exceed 6 ml/min.

3.3.4 After the F-2 fraction has been collected from the column, the flasks are placed in the Turbo-Vap. The apparatus is turned on and Nitrogen gas is introduced to the flasks. The solvent is reduced to approximately 1 ml. The samples are then solvent-exchanged to heptane and concentrated to about 1 ml.

3.3.5 The fractions are then transferred to borosilicate glass vials fitted with Teflon-lined screw caps for storage until analysis.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

4.1 Silica Gel Testing

4.1.1 Silica Gel is verified to separate compound classes using the silica gel testing SOP.

4.2 Method Blanks

4.2.1 Method (procedural) blanks are included in each sample set to provide an estimate of contamination from the reagents.

4.3 Internal Standard Recovery

4.3.1 PCB103 is added to final column fractions to calculate recovery of the internal standard.

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR ANALYSIS OF PAHs BY GC/MS
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard procedure for analyzing marine environmental samples for PAHs using GC/MS in electron impact/positive ion mode.

2.0 EQUIPMENT

HP Model 5890 Series II Gas Chromatograph
HP Model 5971A Mass Selective Detector
HP Model 7673 Autosampler
HP MS Chemstation (DOS Series) Software
IBM Compatible Personal Computer

3.0 OPERATION

A. Instrument Parameters

Column: 60 m x 0.25 mm ID x 0.25 um DB-5 (J&W Scientific)
Carrier: Helium at 25 psi; 0.8-1.0 ml/min
Injector: 270 degrees C; splitless mode, purge on at 0.8 min
Interface: 300 degrees C; direct, source 200 degrees C
Temperature Program: 1 min, 40 deg; 20 deg/min to 120 deg; 10 deg/min to 310 deg and hold 16 min. This is suitable for Polycyclic Aromatic Hydrocarbons.
MS Parameters: Set by Autotune using PFTBA as the calibration compound; Manual Tune is then used to force the 131 and 219 abundances to 20 to 40 percent of the 69 base peak; the electron multiplier is then set to meet the requirements of the particular method. This procedure is done in a series of loops, as new parameter settings for a specific lens will affect the behavior of the others.

B. Daily Performance Checks

1) Adequate DFTPP spectrum (see attached criteria), based on a 50 ng injection.
2) Calibration Check - results for a mid-level standard must be within 25 percent of the true value for a single target compound; the average error for all compounds in the method must be less than 15 percent.

C. Calibration

The calibration method is a 5 point, internal standard, least squares fit, forced through the origin. The levels are chosen to cover a range from 4 to 10 times the instrument detection limit for the lowest point, up to the point at which saturation and/or non-linear behavior is observed. For PAHs in marine sediment or tissue, the current levels are 1.0, 5.0, 10.0, 15.0, and 20.0 ng/ul. Acceptance criteria for each level are the same as listed for the daily check.

D. Sample Analysis

A 250 uL aliquot of the sample extract is blown down to 20-25 uL with nitrogen or helium. If required, an internal injection standard is added (4-chloro-p-terphenyl). Once the daily performance checks are satisfied, the extracts are queued up on the autosampler. Periodic solvent blanks, standards, etc. are inserted at the judgement of the analyst.

E. Identification

Compounds are identified by monitoring a characteristic ion within a 12 second retention time window. Additional ions may be monitored at the discretion of the analyst. Confirmation is obtained by inspection of the full mass spectrum.

4.0 QUALITY ASSURANCE

A. Standard Reference Materials, Blanks, Calibration Checks

Standard reference materials are prepared along with each batch of samples. Calibration standards are verified with independently prepared control standards.

B. Method Detection Limits

Method detection limits are determined independently for a given sample matrix. Instrument detection limits are generally in the 6-10 pg per injection range, which usually corresponds to a 3-5 ng/g (ppb) method detection limit range in samples.

5.0 TROUBLESHOOTING AND MAINTENANCE

On a daily basis, the injection port and liner are cleaned; the septum and glass wool in the liner are changed. It is periodically necessary to break off the first few inches of the column (this is done daily for heavy workloads of dirty samples; compounds most affected are the high molecular weight compounds).

DFTPP ACCEPTANCE CRITERIA (by CLP 3/90)

Mass	Abundance
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Less than mass 443
442	40-60% of mass 198
443	17-23% of mass 442

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR GAS CHROMATOGRAPHIC ANALYSIS OF PCBs AND CHLORINATED PESTICIDES (REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard procedure for analyzing marine environmental samples for polychlorinated biphenyls (PCBs) and chlorinated hydrocarbon pesticides using gas chromatography and electron capture detectors.

2.0 EQUIPMENT USED

Hewlett Packard 5890 Gas Chromatographs equipped with electron capture detectors (Ni 63), automatic samplers, 30 m DB-5 fused silica capillary columns (0.25 μ film thickness, 0.25 mm i.d.). Perkin-Elmer/Nelson software (ACCESS*CHROM) provides for collection and storage of raw chromatographic data, and for selection and quantitation of analyte peaks. Ultra high purity helium and 95/5% Argon/Methane gases are used as the carrier and auxiliary gas respectively.

3.0 OPERATION

3.1 Instrument checks made prior to data collection

3.1.1 Gas supply

3.1.1.1 Check gas cylinder pressures. Replace tank if pressure is less than 100 psig.

3.1.1.2 Check head pressure gauge on front panel of instrument. Gauge should read 18 psig; adjust to correct setting if reading is high; check for leaks if pressure is low. This setting provides for a carrier gas flow of approximately 1.5 ml/min.

3.1.1.3 Replace injection port septum. Check septum nut and column fittings for leaks with leak detector and tighten as necessary.

3.1.1.4 Check the auxiliary gas flow. A flow of 35 ml/min is required.

3.1.1.5 Check septum purge and split flows. Adjust to 1 and 35 ml/min, respectively, as necessary.

3.1.2 Instrument output signal

3.1.2.1 Display the analog output signal from the detector on the LED panel of the GC. Record the value in the instrument log book, and check for consistency with previous readings. On instruments with dual detectors, ensure the signal is correctly assigned to the detector selected for the analysis.

3.1.3 Instrument operating parameters

3.1.3.1 Temperature programs and run times are stored as workfiles in each GC's integrator. The following conditions are required for the analysis of PCBs and pesticides:

Injection port temperature	275°C
Detector temperature	325°C
Initial column temperature	100°C
Initial hold time	1 min
Rate 1	5°C/min
Ramp 1 final temperature	140°C
Ramp 1 hold time	1 min
Rate 2	1.5°C/min
Ramp 2 final temperature	230°C
Ramp 2 hold time	20 min
Rate 3	10°C/min
Final column temperature	300°C
Final hold time	5 min
Stop time	100 min
Injection port purge open time	1 min

3.1.3.2 Load an appropriate workfile into the integrator.

3.1.3.3 Enter the autosampler parameters into the integrator via Option 11. Indicate which injection port is being used, the number and positions of the samples in the autosampler tray, the number of injections per bottle, and the amount injected (1 ul).

3.1.3.4 Check the signal assignments and levels again. If they are correct, store the workfile in the integrator.

3.2 Data system setup

3.2.1 Scheduling of standards and samples

3.2.1.1 Setting up the instrument queue is accomplished by following instructions laid out in the Perkin-Elmer Nelson manual.

3.2.1.2 Order the samples, standards, and rinses according to the following guidelines:

-place hexane rinses before and after standards
-bracket groups of no more than five (5) samples with standards.
-arrange multiple level standards so that a high and a low standard precede as well as follow samples
-procedural and field blanks should be run prior to samples to minimize risk of carryover contamination.

3.2.1.3 Type in sample weight and internal standard amounts for each sample to be used in final concentration calculations. Double check all manually entered values for accuracy.

3.3 Instrument startup and data collection

3.3.1 After the instrument has been scheduled, arrange the samples and standards to be run in the autosampler trays. Check the order for accuracy against a copy of the queue. Load the trays into the autosampler.

3.3.2 Visually recheck tank regulator gauges and instrument settings to ensure proper settings.

3.3.3 Start GC operation and data collection by pressing 'start' on the integrator.

3.4 Peak identification and quantitation

3.4.1 Peak identification is accomplished by automated routines. Identifications are based on comparison of retention times of actual standards to unknown peaks. Multilevel standards are calibrated to generate a linear regression curve of response according to the manufacturer's instructions. After a calibration curve has been generated, the samples are analyzed. Analytes are quantitated based on the peak areas for the analytes and internal standard, the amount of the internal standard, and the response factors generated from the calibration curve. Chromatograms and data reports are generated for each sample and standard.

4.0 QUALITY ASSURANCE

4.1 Chromatograms of standards are compared to posted references. Peak identifications, resolution and shapes are inspected. Calculated standard amounts are checked for accuracy and documented. Other abnormalities, such as spurious or extra peaks, rising or falling baselines, and negative spiking are examined. Response factors

and overall instrument response are compared to previous runs and documented. Blanks are checked for the presence of interferences or analytes of interest. Unknown samples are compared to standards to verify peak identifications.

5.0 TROUBLESHOOTING

5.1 Refer to the ERLN GC Troubleshooting notebook, the manufacturer's manuals, or to experienced personnel for guidance in troubleshooting the GCs.

ERLN CHEMISTRY GROUP STANDARD OPERATING PROCEDURE FOR INSTRUMENTAL ANALYSIS OF METALS IN SEDIMENT AND TISSUE EXTRACTS

1.0 OBJECTIVES

The objective of this document is to outline the proper sample preparation and instrumental parameters for the analysis of trace metals in marine sediment or tissue acid digests.

2.0 MATERIALS AND EQUIPMENT

Atomic Absorption Spectrometer or Inductively Coupled Plasma Atomic Emission Spectrometer

Reagent grade Instra-Analyzed concentrated HNO_3 for trace metal analysis (diluted to 2M concentration)

3.0 METHODS

3.1 Standard Calibration

3.1.1 Estimate or determine the range of concentrations that exist within the sample analytes. This may require scanning several samples prior to standard calibration in order to approximate the range of absorbances (AA) or emission intensities (ICP) produced from the samples.

3.1.2 Prepare multiple calibration standards that bracket the expected range of sample analyte concentrations. The composition of the standard matrices (i.e. acid strength and salt content) should match that in the samples as closely as possible.

3.1.3 Analyze the standards and calculate calibration equations by regression (linear or polynomial) of standard concentrations against measured standard absorbances or intensities.

3.2 Sample Dilutions

3.2.1 In section 3.1 the expected range of sample concentrations is determined. If sample concentrations exceed the upper limit of the chosen analytical technique, then the sample analytes will need to be diluted to fall within the range of standard concentrations. Sample diluent should be of the same acid composition and strength present in the sample analytes (Keep close record of the sample dilutions so that raw analytical concentrations can be dilution-corrected).

4.0 ANALYSIS

4.1 Sample Analysis (Unknown Concentrations)

4.1.1 Analyze the samples and record the absorbances (AA) or emission intensities (ICP).

4.1.2 Triplicate readings should be made for every element.

4.1.3 After approximately 10 (AA) or 20 (ICP) samples, several calibration standards should be re-analyzed to determine instrumental drift.

4.2 Concentration Calculation

4.2.1 Calculate sample concentrations by applying the calibration equation obtained from the standard curve to the measured sample signals (absorbances or intensities). Calculate the mean and standard deviation of the individually calculated sample concentrations.

4.3 Dilution Correction

4.3.1 Calculated analyte concentrations must be dilution- corrected to obtain the true metal concentration present in the sample. The analyte concentration, in ug/ml, is converted to ug/g dry sample by inputing the sample prep. information into the following equation:

$$\text{Sed. Conc. (ug/g dry sed.)} = \frac{\text{Analyte conc.(ug/ml)} \times \text{Acid volume (ml.)}}{\text{dry sed. wt. (g)}}$$

5.0 QUALITY CONTROL

5.1 Determination of Analytical Accuracy (Calibration check)

5.1.1 Analyze several standards as unknown samples to check the accuracy of the standard curve regression. Recoveries should be within 10% of the standard concentration.

5.1.2 Analyze a solution of known and/or certified concentration, prepared independently from the calibration standards, to determine the daily analytical fluctuation. Recoveries should be within 10% of the certified concentration.

5.2 Standard Additions (Spike Additions)

5.2.1 Standard additions are required to investigate instrumental interferences arising from differing sample solution matrices.

5.2.2 Select a sample whose concentrations can be matched fairly closely with a dilution of a calibration standard.

5.2.3 Prepare an acid spike (a dilution of a calibration standard) in the same acid matrix as the samples. Try to match spike concentrations as closely as possible with the sample chosen.

5.2.4 Prepare a sample spike by removing a second sample aliquot and adding the same amount of calibration standard as was used in the acid spike. The total volume of sample spike should also be equal to the total volume of acid used in the acid spike.

5.2.5 Analyze the sample, acid spike and sample spike as unknown samples.

5.2.6 Calculate the spike recovery using the following equation:

$$R(\%) = \frac{C_{\text{SAMPLE SPIKE}} - C_{\text{SAMPLE}}}{C_{\text{ACID SPIKE}}}$$

5.2.7 Acceptable spike recoveries fall between 80-120%

5.2.8 One out of every 20 samples should be chosen for a standard addition.

6.0 DETECTION LIMITS

6.1 Instrument Detection Limits

6.1.1 Instrument detection limits are determined as the concentration equivalent to a signal three times the standard deviation of a blank. The limits should either be determined previously for given instrumental conditions or as part of the instrumental data analysis, and should be comparable to those listed below:

	ICP (ug/ml)	GFAA (ug/L)
Cu	.020	1.0
Zn	.005	0.1
Cr	.020	1.0
Pb	.050	3.0
Ni	.050	2.0
Mn	.010	0.5
Fe	.020	2.0
Cd	.005	0.5
Al	.075	
Sn	.050	2.0
Sb	.100	2.0
As	.100	2.0
Ag	.020	0.5

6.1.2 Sample Detection Limits, assuming a dry weight of 2 grams and a total volume of 50 mls. (ie. sediment ultrasonic extraction method), are 25 times higher than the instrument D.L.'s. Method detection limits should be calculated following the rigorous statistical procedure detailed in 40 CFR Part 136.

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR SEDIMENT EXTRACTION OF SEMIVOLATILE ORGANIC ANALYTES
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard operating procedure for the extraction of semi-volatile organic compounds from marine sediment samples. The extracts will be further cleaned up by silica gel chromatography procedures prior to analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).

2.0 MATERIALS AND EQUIPMENT

Apparatus for homogenizing sediment
Wrist-action shaker
100 ml glass centrifuge tubes
Apparatus for determining weight and dry weight
Top-loading balance capable of weighing to 0.01 g
Aluminum weighing pans
Stainless steel spatula
Drying oven maintained at 105-120°C
Turbo-Vap (Zymark) apparatus, with heated water maintained at 25-35°C
Nitrogen gas, compressed, 99.9% pure
Glass Turbo-Vap flasks, 200 ml
Glass graduated cylinders, 100- and 500-ml
Erlenmeyer flasks, 250 ml
Microliter syringes or micropipets, solvent rinsed
Borosilicate glass vials with Teflon-lined screw caps, 2-ml
Reagents
Methylene chloride, pesticide grade or equivalent
Deionized water, pentane-extracted
Acetone, pesticide grade or equivalent
Sodium sulfate-anhydrous, reagent grade. Heated to 400°C for at least 4 hours, then cooled and stored in a tightly sealed glass container at room temperature.
Internal Standards, to be added to each sample prior to extraction.

3.0 METHODS

3.1 Find the correct caps for each centrifuge tube to be used by filling them with

approximately 25 mls of methylene chloride, putting the caps on and rolling the tube on the lab bench on a paper towel and look for leaks. Once the correct tubes and caps have been matched, weigh approximately 10.0 g of homogenized sample into a solvent rinsed centrifuge tube. Homogenization is accomplished by physical mixing of the sediment with stainless steel or Teflon coated utensils, or by a polyethylene propeller attached to an electric drill. The amount of sample may be adjusted based on expected contaminant concentrations or detection limits required. Weigh approximately 2.0 grams into a preweighed aluminum pan for dry/wet determination.

3.2 Add Internal Standards as required: CB198 for PCB analysis, 2,5-dichloro-m-terphenyl for pesticides, and d12 Benzo(a)anthracene/ d10 Phenanthrene mix for PAHs. The amount of IS added is dependent on the expected contaminant concentrations and should be equivalent to those concentrations.

3.3 Add 30 g Sodium sulfate and mix with a teflon coated spatula very well. Then add 50 ml 20:80 acetone:methylene chloride.

3.4 Seal the centrifuge tubes with teflon tape and caps, and shake ~ 15 hrs. (overnight). Shake tubes at approximately a 60° angle, at an intensity setting of "5". Centrifuge for 20 minutes at 1750 rpm and pour off the supernatant into an erlenmeyer flask.

3.5 Add 50 ml of 20:80 acetone:methylene chloride, seal and shake as above for ~ 6 hrs. Centrifuge for 20 minutes at 1750 rpm and add the supernatant to the erlenmeyer flask. Add some additional sodium sulfate to the combined extracts to ensure all water is excluded.

3.6 Gravity filter the extract through a pre-rinsed (methylene chloride) glass fiber filter. Rinse the erlenmeyer 2 x with methylene chloride, and the filter itself once. Collect the filtrate in a clean rinsed 200 ml Turbo-Vap tube. Place the flask into the Turbo-Vap apparatus, and turn on the unit. Open the valve on the nitrogen tank and adjust the regulator to ensure a pressure of 15 psi. Reduce the sample volume to approximately 1 ml, with solvent exchange to pentane.

3.9 Adjust the volume to 1 ml with hexane.

3.10 Fractionate the sample following the Column Chromatography SOP.

4.0 OPTIONAL CLEANUP PROCEDURES

Activated copper powder (activated by the addition of 8 M hydrochloric acid and rinsed with the following solvents in succession: deionized water, methanol, methylene chloride, and hexane) may be added to the extract to remove any free elemental sulfur. The copper is added until the formation of black copper sulfide no longer occurs.

5.0 QUALITY ASSURANCE/QUALITY CONTROL

5.1 Standard Reference Materials

5.1.1 A certified SRM is prepared with each batch of samples to validate analytical recovery. Results are compared to certified concentrations and corrective action is required if the accuracy is outside of the required specifications.

5.1.2 SRMs should be prepared in the exact same manner as the unknowns.

5.2 Analytical Reproducibility

5.2.1 Replicate samples should be prepared to assess the reproducibility of the extraction procedure.

5.2.2 For every batch of samples, one sample should be chosen to extract and analyze in triplicate. Deviation between replicate samples should be $<30\%$.

5.3 Procedural Blanks

5.3.1 Procedural blanks should be carried throughout the entire extraction procedure to verify the absence of contamination of the method.

5.3.2 Trace amounts of analytes in the blanks (less than three times the method detection limit) may be ignored and have no effect on the subsequent sample analyses, but samples should be rejected if significant concentrations (greater than five times the MDL) are present in procedural blanks.

5.3.3 One blank should be prepared for each batch of samples (minimum frequency of 5%).

ERLN CHEMISTRY GROUP STANDARD OPERATING PROCEDURE FOR DIGESTION OF MARINE ORGANISM SAMPLES FOR METALS ANALYSIS

1.0 OBJECTIVES

The objective of this document is to establish the standard operating procedure for the total digestion of marine tissue samples. Sample extracts are routinely analyzed by Flame Atomic Absorption Spectrometry (FAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

2.0 MATERIALS AND EQUIPMENT

Top-loading balance (0.01 gram precision)
Vacuum Freeze Dryer
CEM Microwave Digestion System (Including 100 ml. Teflon vessel liners and pressure control capability)
50 ml. class A volumetric flasks
60 ml. polyethylene screw-cap bottles
Instra-Analyzed grade concentrated HNO_3 for trace metal analysis (70-71 %)
Hydrogen Peroxide - H_2O_2 (30%)
Vacuum filtering apparatus with Whatman 42 filter paper

3.0 METHODS

3.1 Sample Preparation

3.1.1 Organism samples should be thawed, and handled only with plastic or stainless steel utensils. Where neccessary, organism tissues should be homogenized. If chromium or nickel is to be analyzed in the samples, the homogenizer tip should be constructed of titanium to avoid contamination of sample tissues.

3.1.2 Obtain the tare weight of labeled, acid-washed 100 ml. Teflon microwave digestion vessel liners.

3.1.3 Weigh approximately 3-5 grams wet tissue into each vessel (~0.5 grams dry). Obtain the wet gross weight of each tube.

3.1.4 Freeze dry samples and obtain the dry gross weight for each sample. Subtract the tare weight and record the weight of dry tissue in each tube.

3.2 Closed Vessel Microwave Digestion (1st Stage)

3.2.1 Add 10 ml. of concentrated HNO_3 (70-71 %) to each digestion vessel.

3.2.2 Make sure the tissue sample is fully saturated and allow to sit for a minimum of 1 hour, or until all foaming subsides.

3.2.3 Place each liner into a microwave vessel.

3.2.4 Insert a pressure relief membrane into each cap assembly and place on top of the vessels. (use the modified cap assembly for the vessel to be used for pressure monitoring)

3.2.5 Place a top on each vessel and hand tighten.

3.2.6 Place the vessels into the carousel.

3.2.7 Insert a vent tube into each vessel, place the free end in the center trap, then place the carousel into the oven.

3.2.8 Connect the pressure sensing line to the modified cap assembly. (make sure the valve on the side of the oven is in the "neutral" position)

3.2.9 Program the oven following the parameters below:

STAGE	1	2	3	4	5
%POWER	85	85	85	85	85
PSI	20	40	85	150	190
TIME	15:00	15:00	15:00	15:00	15:00
TAP	5:00	5:00	5:00	5:00	5:00
FAN SPEED	100	100	100	100	100

** Note - Power settings are for 12 vessels. If a different # of vessels is desired, subtract or add 5% power per vessel.

3.2.10 After completion of the program, allow the pressure in the control vessel to drop below 20 PSI, then manually vent the control vessel, remove the pressure sensing line and place the carousel into the fume hood.

3.3 Closed Vessel Microwave Digestion (2nd Stage)

3.3.1 Manually vent each vessel, remove the caps and add 2 ml. of 30% H_2O_2.

3.3.2 Allow the reaction to subside, then reassemble the vessels as described in

sections 3.2.4-3.2.6.

3.3.3 Place the carousel into the oven and reconnect the pressure sensing line to the control vessel. Check to ensure the exhaust fan is operating.

3.3.5 Program the oven following the parameters below:

STAGE	1	2
%POWER	85	100
PSI	100	100
TIME	15:00	15:00
TAP	5:00	5:00
FAN SPEED	100	100

** Note - Power settings are for 12 vessels. If a different # of vessels is desired, subtract or add 5% power per vessel.

3.3.6 Although the oven is automated, individual tissue samples will react differently, so all steps should be monitored in case venting should occur. If venting does occur, remove the vented vessels and lower the power accordingly.

3.3.7 After completion of the program, allow the vessels to cool in the oven until the pressure in the control vessel is below 20 PSI.

3.3.8 Manually vent the control vessel, then remove the carousel and place in a fume hood until the liquid reaches room temperature.

3.3.9 Remove the vent tubes and manually vent the remaining vessels.

3.4 Sample Filtration

3.4.1 Remove the tops and rinse the lids with deionized water, catching the rinse in the vessel liner.

3.4.2 Add ~15 ml. of deionized water to each vessel.

3.4.3 Using plastic tweezers, place a sheet of Whatman 42 filter paper in a vacuum filtration funnel and wet the paper with 2M HNO_3.

3.4.4 Place a 60 ml. acid-cleaned polyethylene bottle and vacuum gasket under the filter funnel and apply vacuum.

3.4.5 Filter the digested sample through the paper and collect the filtrate in the

bottle.

3.4.6 Rinse the digestion vessel with deionized water, filter and collect the filtrate in the bottle.

3.4.7 Pour the combined filtrates into a 50 ml. acid-cleaned volumetric flask, and dilute to the mark with deionized water.

3.4.8 Shake the solution thoroughly and transfer back to the acid-cleaned 60 ml. polyethylene bottle. Label the bottle appropriately.

4.0 QUALITY ASSURANCE

4.1 Standard Reference Materials (SRM)

4.1.1 A certified SRM should be prepared with every batch of samples to validate analytical recovery.

4.1.2 SRMs should be prepared in the exact manner as the unknown samples, including drying, even if the material is already dry.

4.1.3 The frequency of SRM preparation should be approximately 1 for every 20 unknown samples prepared.

4.1.4 The outlined extraction technique should yield close to 100% recoveries for organism SRMs, as outlined in the ERLN QA/QC guidelines.

4.2 Analytical Reproducibility

4.2.1 Replicate samples should be prepared to assess the reproducibility of the digestion procedure.

4.2.2 For every 20 samples prepared, one sample should be chosen to digest and analyze in triplicate. The relative standard deviation between replicate analyses should be <20%.

4.3 Procedural Blanks

4.3.1 Procedural blanks should be carried throughout the entire extraction procedure to verify that contaminants are not present in the reagents and that no contamination has occurred throughout the procedure.

4.3.2 Trace amounts of metals in the blanks can be subtracted from subsequent sample analyses (blank subtraction), but a sample batch should be rejected if concentrations in the blank are >10% of "average" sample concentrations.

4.3.3 One procedural blank should be prepared for every 20 samples extracted.

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR TOTAL DIGESTION OF SEDIMENT SAMPLES

1.0 OBJECTIVES

The objective of this document is to establish the standard operating procedure for the total digestion of bulk sediments. Sample digests are routinely analyzed by Flame Atomic Absorption Spectrometry (FAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP).

2.0 MATERIALS AND EQUIPMENT

Top-loading balance (0.01 gram precision)
Vacuum Freeze Dryer
CEM Microwave Digestion System (Including 100 ml. Teflon digestion vessel liners with pressure control capability)
Protective Clothing (Polyethylene apron, Neoprene gloves, Safety goggles, Face shield)
100 ml. class A volumetric flasks
125 ml. polyethylene screw-cap bottles
Instra-Analyzed grade concentrated HNO_3 for trace metal analysis (70-71 %)
Reagent grade concentrated HF (49%)
Reagent grade concentrated HCL (36.5-38%)
Boric Acid (5%) prepared from H_3BO_3 crystals
Deionized water

3.0 METHODS

3.1 Sample Preparation

3.1.1 Sediment samples should be thawed and homogenized with plastic or stainless steel utensils.

3.1.2 Obtain the tare weight of labeled, acid-washed 100 ml. Teflon microwave digestion vessels liners.

3.1.3 Weigh approximately 1.5 grams wet sediment into each vessel (~0.5 grams dry). Obtain the wet gross weight of each liner.

3.1.4 Freeze dry samples and obtain the dry gross weight for each sample. Subtract the tare weight and record the weight of dry sediment in each liner.

3.2 Microwave digestion

** NOTE- Be sure to wear proper safety clothing when working with the concentrated HF.

3.2.1 Add 5 ml. of concentrated HNO_3 (70-71 %), 4 ml. of concentrated HF (49%) and 1 ml. concentrated HCl (36.5-38%) to the vessel liners.

3.2.2 Make sure the sediment is fully saturated and allow to sit for a minimum of 1 hour.

3.2.3 Place the liners into their corresponding vessels.

3.2.4 Insert a rupture membrane into each lid and secure into place with a cap. Do not overtighten.

3.2.5 Place the vessels into the carousel.

3.2.6 Insert a vent tube into each vessel and place the free end into the center trap.

3.2.7 Attach the pressure sensing line to thhe control vessel, making sure the lever on the side of the oven is in the "neutral" position.

3.2.8 Program the oven following the parameters below:

STAGE	1	2
%POWER	100	100
PSI	120	150
TIME	30:00	15:00
TAP	20:00	10:00
FAN SPEED	100	100

**Note - Power settings are for 12 vessels. If a different # of vessels is desired, subtract or add 5% power per vessel.

3.2.9 Although the oven is automated, individual sediments will react differently, so all steps should be monitored in case venting should occur. If venting does occur, remove the vented vessels and lower the power accordingly.

3.2.10 When the program is finished, allow the pressure in the control vessel to drop below 20 PSI.

3.2.11 Manually vent the control vessel, detach the pressure sensing line and place the carousel in a fume hood.

3.2.12 Remove the vent tubes and vent the remaining vessels manually.

3.2.13 In a fume hood, remove the caps and rinse the lids with deionized water, catching the rinse in the vessel liner.

3.2.14 Add 30 ml. of 5% Boric acid to each sample.

3.3 Sample Filtration (This step may not be necessary)

3.3.1 Add ~15 ml. of deionized water to each vessel.

3.4.2 Using plastic tweezers, place a sheet of Whatman 42 filter paper in a vacuum filtration funnel and wet the paper with 2M HNO_3.

3.3.3 Place a 120 ml. acid-cleaned polyethylene bottle and vacuum gasket under the filter funnel and apply vacuum.

3.3.4 Filter the digested sample through the paper and collect the filtrate in the bottle.

3.3.5 Rinse the digestion vessel with deionized water, filter and collect the filtrate in the bottle.

3.3.6 Pour the combined filtrates into a 100 ml. acid-cleaned volumetric flask, and dilute to the mark with deionized water.

3.3.7 Shake the solution thoroughly and transfer back to the acid-cleaned 120 ml. polyethylene bottle. Label the bottle appropriately.

3.4 Sample Dilution (Required only if filtration step was omitted)

3.4.1 Transfer the contents of the vessel liner to a clean 100 ml. volumetric flask and rinse the vessel with deionized water, also adding the rinse to the flask.

3.4.2 Dilute to the volume mark with deionized water.

3.4.3 Shake the extracts thoroughly and transfer into acid-cleaned 125 ml. polyethylene screw-cap bottles.

3.4.4 Label the bottles appropriately and store at room temperature until analysis.

4.0 QUALITY ASSURANCE

4.1 Standard Reference Materials (SRMs)

4.1.1 A certified SRM should be prepared with every batch of samples to validate analytical recovery.

4.1.2 SRMs should be prepared in the exact manner as the unknown samples, including drying, even if the material is already dry.

4.1.3 The frequency of SRM preparation should be approximately 1 for every 20 unknown samples prepared.

4.1.4 The outlined extraction technique should yield close to 100% recoveries for sediment SRMs.

4.2 Analytical Reproducibility

4.2.1 Replicate samples should be prepared to assess the reproducibility of the digestion procedure.

4.2.2 For every 20 samples prepared, one sample should be chosen to digest and analyze in triplicate. The relative standard deviation between replicate analyses should be <20%.

4.3 Procedural Blanks

4.3.1 Procedural blanks should be carried throughout the entire digestion procedure to verify that contaminants are not present in the reagents and that contamination has not occurred throughout the procedure.

4.3.2 Trace amounts of metals in the blanks can be subtracted from subsequent sample analyses (blank subtraction), but a sample batch should be rejected if concentrations in the blank are >10% of "average" sample concentrations.

4.3.3 One procedural blank should be prepared for every 20 samples digested.

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR TISSUE EXTRACTION OF SEMIVOLATILE ORGANIC ANALYTES
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard operating procedure for the extraction of semi-volatile organic compounds from marine tissue samples. The extracts will be further cleaned up by silica gel chromatography procedures prior to analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).

2.0 MATERIALS AND EQUIPMENT

Apparatus for homogenizing tissue
- Brinkman Polytron
- 100- or 150-ml glass centrifuge tubes

Apparatus for determining weight and dry weight
- Top-loading balance capable of weighing to 0.01 g
- Aluminum weighing pans
- Stainless steel spatula

Drying oven maintained at 105-120°C

Turbo-Vap (Zymark) apparatus, with heated water bath maintained at 25-35° C
- Nitrogen gas, compressed, 99.9% pure
- Glass Turbo-vap flasks, 200 ml

Glass graduated cylinders, 100- and 500-ml
Glass separatory funnels, 1 L.
Glass erlenmeyer flasks, 250 and 500 ml.
Borosilicate glass vials with Teflon-lined screw caps, 2-ml

Microliter syringes or micropipets, solvent rinsed

Reagents
- Pentane, pesticide grade or equivalent
- Acetonitrile, pesticide grade or equivalent
- Deionized water, pentane-extracted
- Sodium sulfate-anhydrous, reagent grade. Heated to 400°C for at least 4 hours, then cooled and stored in a tightly-sealed glass container at room

temperature.

Internal Standards, to be added to each sample prior to extraction.

3.0 METHODS

3.1 Weigh approximately 10.0 g of sample into a solvent rinsed centrifuge tube. Weigh approximately 1.0 gram into a preweighed aluminum pan for dry/wet determination.

3.2 Add Internal Standards as required: CB198 for PCB analysis, 2,5-dichloro-m-terphenyl for pesticides, and d12 Benzo(a)Anthracene and d10 Phenanthrene mix for PAHs. The amount of IS added is dependent on the expected contaminant concentrations and should be equivalent to those concentrations.

3.3 Add 50 ml acetonitrile.

3.4 Polytron the samples for 20 seconds, at a speed setting of ~ 5. Centrifuge for 10 minutes at 1750 rpm and pour off the supernatant into a separatory funnel containing 500 ml pentane extracted deionized water (DI). Repeat this step two more times.

3.5 Back extract the DI/ACETONITRILE phase in the separatory funnel with 3 X 50 ml pentane. After each addition of pentane has been shaken, draw off the bottom layer into a 500 ml erlenmeyer flask. Decant the Pentane layer into a 250 ml erlenmeyer flask by pouring it out the top of the separatory funnel. This way the transfer of water into the pentane extract will be avoided.

3.6 Transfer the water layer from the 500 ml erlenmeyer flask back into the separatory funnel for every addition of pentane. Rinse the 500 ml flask 3 x with Pentane and add the rinses to the separatory funnel.

3.7 Combine the pentane extracts and dry over Sodium Sulfate.

3.8 Transfer the sample to a 200 ml Turbo-Vap flask. Rinse the flask 3 x with pentane and add the rinses to the flask. Place the flask into the Turbo-Vap apparatus, and turn on the unit. Open the valve on the nitrogen tank and set the regulator to ensure a pressure of 15 psig is reaching the Turbo-Vap unit. Reduce the volume of sample to approximately 1 ml.

3.9 Adjust the volume to 1.0 ml with pentane. Remove 0.1 ml of sample into a preweighed aluminum pan for lipid weight determination. Allow it to dry at room temperature for at least 24 hours. Record the weight of the pan plus the sample.

3.10 Fractionate the sample following the Column Chromatography SOP.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

4.1 Standard Reference Materials

4.1.1 A certified SRM is prepared with each batch of samples to validate analytical recovery. Analytical results should then be compared to the certified concentrations. Corrective action is required if the required accuracy goals are not met.

4.1.2 SRMs should be prepared in the exact same manner as the unknowns.

4.2 Analytical Reproducibility

4.2.1 Replicate samples should be prepared to assess the reproducibility of the extraction procedure.

4.2.2 For every batch of samples, one sample should be chosen to extract and analyze in triplicate. Deviation between replicate samples should be $<30\%$.

4.3 Procedural Blanks

4.3.1 Procedural blanks should be carried throughout the entire extraction procedure to verify the absence of contamination of the method.

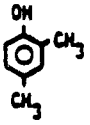
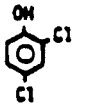
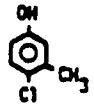
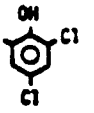
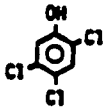
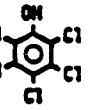
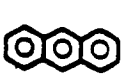
4.3.2 Trace amounts of analytes in the blanks (less than three times the method detection limit) may be ignored and have no effect on the subsequent sample analyses, but samples should be rejected if significant concentrations (greater than five times the MDL) are present in procedural blanks.

4.3.3 One blank should be prepared for each batch of samples (minimum frequency 5%).

APPENDIX E

EPA Priority Pollutants and Additional Hazardous Substance List Compounds

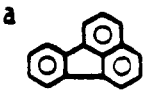
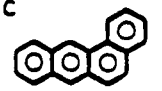
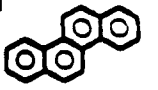
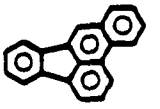
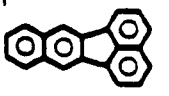
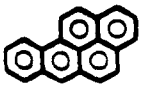
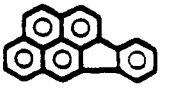
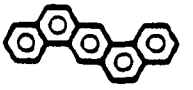
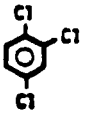
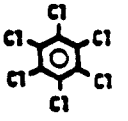
CHEMICAL STRUCTURES AND MOLECULAR WEIGHTS OF U.S. EPA PRIORITY POLLUTANT AND ADDITIONAL HAZARDOUS SUBSTANCE LIST COMPOUNDS

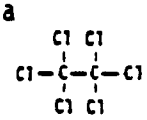
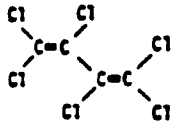
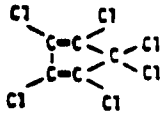
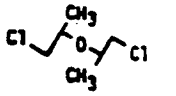
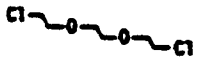
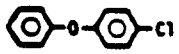
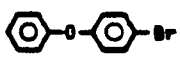
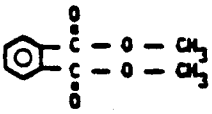
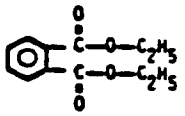
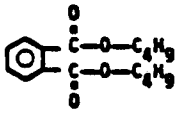
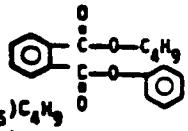
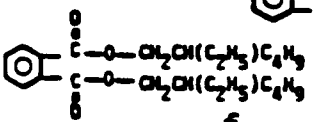
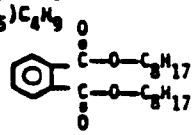
	EPA #	Compound	Structure	mw
PHENOLS				
a	65	phenol		94
b	HSL	2-methylphenol		108
c	HSL	4-methylphenol		108
d	34	2,4-dimethylphenol		122
SUBSTITUTED PHENOLS				
a	24	2-chlorophenol		126
b	31	2,4-dichlorophenol		163
c	22	4-chloro-3-methylphenol		143
d	21	2,4,6-trichlorophenol		198
e	HSL	2,4,5-trichlorophenol		198
f	64	pentachlorophenol		266
g	57	2-nitrophenol		139
h	59	2,4-dinitrophenol		184
LOW MOLECULAR WEIGHT AROMATICS				
a	55	naphthalene		128
b	77	acenaphthylene		152
c	1	acenaphthene		154
d	80	fluorene		116
e	81	phenanthrene		178
f	78	anthracene		178

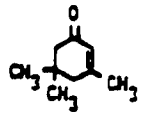
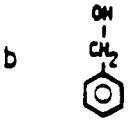
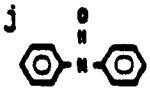
EPA # - EPA priority pollutant number defined for toxic pollutants in 40 CFR 401.15 that are a subset of the hazardous substances listed in Appendix VIII of 40 CFR 261.

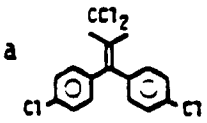
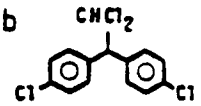
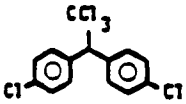
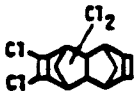
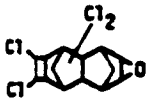
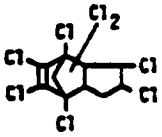
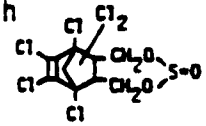
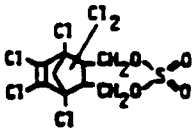
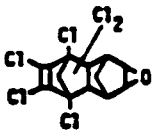
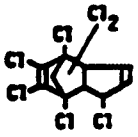
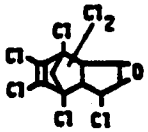
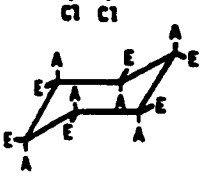
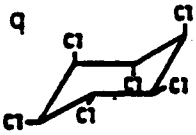
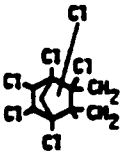
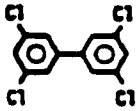
mw - molecular weight of an organic compound.

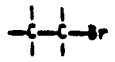
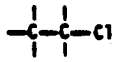
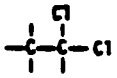
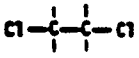
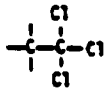
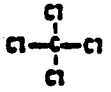
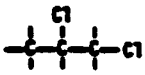
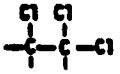
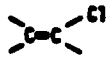
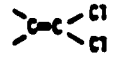
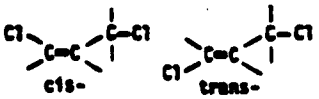
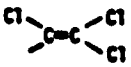
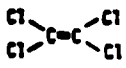
HSL - hazardous substance list.

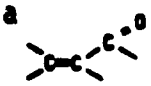
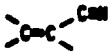
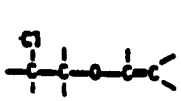
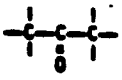
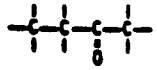
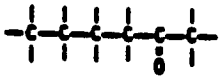
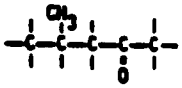
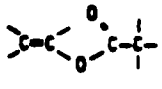
	EPA #	Compound	Structure	mw
HIGH MOLECULAR WEIGHT PAH				
a	39	fluoranthene		202
b	84	pyrene		202
c	72	benzo(a)anthracene		228
d	76	chrysene		228
e	74	benzo(b)fluoranthene		252
f	75	benzo(k)fluoranthene		252
g	73	benzo(a)pyrene		252
h	83	indeno(1,2,3-c,d)pyrene		276
i	82	dibenzo(a,h)anthracene		278
j	79	benzo(g,h,i)perylene		276
CHLORINATED AROMATIC HYDROCARBONS				
a	26	1,3-dichlorobenzene		147
b	27	1,4-dichlorobenzene		147
c	25	1,2-dichlorobenzene		147
d	8	1,2,4-trichlorobenzene		181
e	20	2-chloronaphthalene		163
f	9	hexachlorobenzene		285

	EPA #	Compound	Stucture	mw
CHLORINATED ALIPHATIC HYDROCARBONS				
a	12	hexachloroethane		168
b	xx	trichlorobutadiene isomers		158
c	xx	tetrachlorobutadiene isomers	b,c,d: 	192
d	xx	pentachlorobutadiene isomers		226
e	52	hexachlorobutadiene	e 	261
f	53	hexachlorocyclopentadiene	f 	273
HALOGENATED ETHERS				
a	18	bis(2-chloroethyl)ether	a  b 	143
b	42	bis(2-chloroisopropyl)ether	c 	171
c	43	bis(2-chloroethoxy)methane	d 	173
d	40	4-chlorophenyl phenyl ether	e 	204
e	41	4-bromophenyl phenyl ether		249
PHTHALATES				
a	71	dimethyl phthalate	a 	194
b	70	diethyl phthalate	b 	222
c	68	di-n-butyl phthalate	c 	278
d	67	butylbenzylphthalate	d 	312
e	66	bis(2-ethylhexyl) phthalate	e 	391
f	69	di-n-octylphthalate	f 	391

	EPA #	Compound	Structure	mw
MISCELLANEOUS OXYGENATED COMPOUNDS				
a	54	isophorone		138
b	HSL	benzyl alcohol		108
c	HSL	benzoic acid		122
d	129	2,3,7,8-tetrachlorodibenzo-p-dioxin		322
e	HSL	dibenzofuran		168
ORGANONITROGEN COMPOUNDS				
a	HSL	aniline		98
b	56	nitrobenzene		123
c	63	N-nitroso-di-n-propylamine		130
d	HSL	4-chloroaniline		128
e	HSL	2-nitroaniline		138
f	HSL	3-nitroaniline		138
g	HSL	4-nitroaniline		138
h	36	2,6-dinitrotoluene		182
i	35	2,4-dinitrotoluene		182
j	62	N-nitrosodiphenylamine		198
k	5	benzidine		184
l	28	3,3'-dichlorobenzidine		253

	EPA #	Compound	Structure	mw
PESTICIDES				
a	93	p,p'-DDE		318
b	94	p,p'-DDD		320
c	92	p,p'-DDT		356
d	89	aldrin		365
e	90	dieldrin		381
f	91	chlordane		410
g	95	alpha-endosulfan *		407
h	96	beta-endosulfan *	*ISOMERS HAVE DIFFERENT RING ORIENTATIONS	407
i	97	endosulfan sulfate		423
j	98	endrin		381
k	99	endrin aldehyde	STRUCTURE NOT SHOWN	381
l	100	heptachlor		373
m	101	heptachlorepoxide		389
n	102	alpha-HCH	A = AXIAL E = EQUATORIAL α - HCH: 4 EQUATORIAL Cl β - HCH: 6 EQUATORIAL Cl δ - HCH: 5 EQUATORIAL Cl	290
o	103	beta-HCH		
p	104	delta-HCH		
q	105	gamma-HCH	 3 EQUATORIAL Cl 3 AXIAL Cl	290
r	113	toxaphene	 (MANY COMPONENTS, APPROXIMATE FORMULA)	
PCBs				
a	106	Aroclor 1242	 REPRESENTATIVE FORMULA	
b	110	Aroclor 1248		
c	107	Aroclor 1254		
d	111	Aroclor 1260		

	EPA #	Compound	Structure	mw
VOLATILE HALOGENATED ALKANES				
a	45	chloromethane		50.6
b	46	bromoethane		109
c	16	chloroethane		64.5
d	44	methylene chloride		85
e	13	1,1'-dichloroethane		99
f	23	chloroform		119
g	10	1,2-dichloroethane		99
h	11	1,1,1-trichloroethane		133
i	6	carbon tetrachloride		154
j	48	bromodichloromethane		164
k	32	1,2-dichloropropane		133
l	51	chlorodibromomethane		208
m	14	1,1,2-trichloroethane		133
n	47	bromoform		253
o	15	1,1,2,2-tetrachloroethane		168
VOLATILE HALOGENATED ALKENES				
a	88	vinyl chloride		62.5
b	29	1,1'-dichloroethene		97
c	30	trans-1,2-dichloroethene		97
d	33	cis- and trans-1,3-dichloropropene		111
e	87	trichloroethene		131
f	85	tetrachloroethene		166

	EPA #	Compound	Structure	mw
VOLATILE AROMATIC HYDROCARBONS				
a	4	benzene	a 	78
b	86	toluene	b 	92
c	38	ethylbenzene	c 	106
d	HSL	styrene	d 	104
e	NSL	total xylenes	e  e.g. AND OTHER ISOMERS	106
VOLATILE CHLORINATED AROMATIC HYDROCARBONS				
a	7	chlorobenzene	a 	112
VOLATILE UNSATURATED CARBONYL COMPOUNDS				
a	2	acrolein	a 	56
b	3	acrylonitrile	b 	53
VOLATILE ETHERS				
a	19	2-chloroethylvinylether	a 	106
VOLATILE KETONES				
a	HSL	acetone	a 	58
b	HSL	2-butanone	b 	72
c	HSL	2-hexanone	c 	100
d	HSL	4-methyl-2-pentanone	d 	100
MISCELLANEOUS VOLATILE COMPOUNDS				
a	HSL	carbon disulfide	a 	76
b	HSL	vinyl acetate	b 	86

APPENDIX F

Example Quality Assurance Reports

PREFACE

The following examples of detailed quality assurance (QA) reviews for a metals data package and a polychlorinated biphenyl (PCB) data package demonstrate the kind of information provided by QA specialists. The sections of these example reports address each of the components of a QA review discussed in Section 2.16 in the main text of this document.

These reviews were conducted in accordance with EPA Contract Laboratory Program procedures. QA reviews for other programs may use alternative criteria for evaluation and different detection limits. For example, the target detection limits discussed for dredging programs differ from the detection limits described in this QA review.

CONTENTS

QUALITY ASSURANCE REVIEW OF METALS IN WATER SAMPLES

INTRODUCTION

This report documents the results of a quality assurance review of analytical data for metals in water samples from Project X. This quality assurance report is provided in support of the quality assurance project plan for this project.

All laboratory analyses were performed by Analysis Laboratory in City, State. All samples were analyzed in accordance with the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program Statement of Work for Inorganic Analyses (U.S. EPA 1987). Data validation was performed according to EPA's *Laboratory Data Validation: Functional Guidelines for Evaluating Inorganics Analyses* (U.S. EPA 1988).

The quality assurance review included examination and validation of the following laboratory data:

- Sample digestion and extraction logs
- All instrument printouts, except for mercury (the instrument printout was not available from the laboratory)
- Instrument calibration and calibration verification procedures and results
- Sample holding times and custody records
- Manual data transcriptions and computer algorithms.

Data qualifiers were assigned as necessary during this review. Following the validation procedures, data quality was assessed with respect to accuracy, precision, and completeness. All qualifier codes used in this report are defined in Table F-1.

QUALITY ASSURANCE REVIEW

Overall Case Assessment

All data for metals in the five water samples are acceptable as qualified in this review for the uses specified in the quality assurance project plan except for the matrix spike result for silver, which was rejected. Data for all samples analyzed for cadmium, calcium, lead, mercury, silver, and zinc are acceptable as estimates. Data qualified as *J* (estimated) are

TABLE F-1. DATA QUALIFIER CODES

Qualifiers Applied During Quality Assurance Review

U The analyte was not present above the level of the associated value. The associated numerical value indicates the approximate concentration necessary to detect the analyte in this sample.

J The analyte was positively identified, but the associated numerical value may not be consistent with the amount actually present in the field sample. The data should be seriously considered for decision-making and are usable for many purposes.

UJ The analyte was not present above the level of the associated numerical value. The associated numerical value may not accurately or precisely represent the concentration necessary to detect the analyte in this sample.

R The data are unusable for all purposes. The presence or absence of the analyte has not been verified. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

Qualifiers Applied During Laboratory Validation[a]

E The reported value is estimated because of the presence of interference. This qualifier is commonly used when the serial dilution result for analyses by inductively coupled plasma-atomic emission spectrometry (ICP) does not meet control limits.

M Duplicate injection precision was not met.

N Predigestion matrix recovery was not within control limits.

S The reported value was determined by the method of standard additions (MSA). The associated value is as reliable as unqualified results.

W The postdigestion spike recovery for GFAA[b] analysis was not within control limits (85–115 percent), and the sample absorbance was less than 50 percent of the spike absorbance.

***** Duplicate analysis was not within control limits.

+ The reported value was determined by MSA. The correlation coefficient for MSA is < 0.995.

[a] Adapted from U.S. EPA (1987).

[b] Graphite furnace atomic absorption spectrometry.

acceptable, but a greater degree of uncertainty is associated with these values than with unqualified data.

The matrix spike result for silver was rejected because the postdigestion spike recovery (58 percent) was well below the EPA Contract Laboratory Program (CLP) control limit (85- to 115-percent recovery). Analysis of the sample by the method of standard additions (MSA) is required in this case, but was not performed.

Calcium values received *J* qualifiers because the CLP control limit (U.S. EPA 1987) was exceeded slightly for the serial dilution sample analyzed by inductively coupled plasma-atomic emission spectrometry (ICP). Reported results may be underestimated by approximately 10 percent.

Cadmium and lead results received *J* qualifiers because CLP control limits for matrix spike recoveries and for duplicate analyses were exceeded. In addition, the result for lead in Sample 2 was restated as undetected (*U*) at the reported concentration because the associated digestion blank was contaminated. Cadmium and lead data should be considered order-of-magnitude estimates.

Mercury results were qualified *J* because the matrix spike recovery was below the CLP control limit. These results may be 100–200 percent higher than reported.

A *J* qualifier was applied to silver results because recovery of silver was poor for the laboratory control sample (LCS). Silver results may be approximately 100 percent higher than reported. Additional individual results were qualified *J* because the correlation coefficient for the results determined by MSA did not meet the CLP control limit of 0.995

The overall data quality achieved by the laboratory for analyses completed by ICP (Table F-2) is typical for metals analyses in water samples. The overall data quality for analyses by graphite furnace atomic absorption (GFAA) is typical for arsenic, chromium, and silver. Data quality for cadmium, lead, and mercury is less than may be expected for these analytes in similar samples. Data quality may have been affected by unstable instrument performance.

Completeness

A complete data package was submitted by the laboratory for five water samples, one matrix duplicate and one matrix spike, and one laboratory control sample and one method blank for each digestion batch. A list of analytes is included in Table F-2. During the quality assurance review, 33 results were qualified *J* as discussed above. Data completeness for metals was 100 percent of total requested analytes.

TABLE F-2. ANALYTICAL METHODS AND INSTRUMENT DETECTION LIMITS

Analyte	Method of Analysis	Instrument Detection Limit (µg/L)
Aluminum	ICP[a]	55
Arsenic	GFAA[b]	5
Cadmium	GFAA	5
Calcium	ICP	28
Chromium	GFAA	10
Copper	ICP	11
Iron	ICP	9.6
Lead	GFAA	5
Magnesium	ICP	140
Manganese	ICP	1.8
Mercury	CVAA[c]	0.2
Nickel	ICP	18
Silver	GFAA	5
Zinc	ICP	4

[a] Inductively coupled plasma-atomic emission spectrometry.

[b] Graphite furnace atomic absorption spectrometry.

[c] Cold vapor atomic absorption spectrometry.

[d] Manual spectrophotometry.

Holding Times

Holding times required by EPA CLP protocols were met for all metals analyses.

Analytical Methods

All sample digestion and analysis procedures, instrument calibration procedures, and quality control checks conformed to EPA CLP requirements except as noted below.

Sample Preparation and Analysis

Water samples were digested according to requirements specified for CLP (U.S. EPA 1987). Sample digestates were analyzed by ICP, GFAA, and cold vapor atomic absorption spectrometry (CVAA), as indicated in Table F-2. Multiple digestions were prepared for Samples 1 and 2 and the duplicate and the spike of Sample 2, because unacceptably high levels of lead were present in the second preparation blank and because volumes of digestate were initially insufficient for all analyses. A preparation blank and a laboratory control sample were digested and analyzed with each batch. Only lead and arsenic results were obtained from the second and third digestion batches. Results for all applicable quality control samples, except the method blank for lead for the third digestion group, were provided on the appropriate CLP forms by the laboratory or were added during the quality assurance review.

Instrument Calibration

Instrument calibration was completed according to EPA CLP protocols (U.S. EPA 1987). Four calibration standards and one blank were used for all analyses by GFAA. The correlation coefficient of a least squares linear regression met the CLP control limit of ≥ 0.995 in all cases except one. The correlation coefficient was 0.993 for the initial calibration for analysis of cadmium in Samples 3 and 5. Consequently, the cadmium results for these samples were qualified *J*.

ICP instruments were calibrated according to manufacturer instructions, using one standard and one blank. A low-level standard was used to verify accuracy of the calibration curve at low analyte concentrations for all metals except mercury and aluminum.

Initial (ICV) and continuing (CCV) calibration check standards and initial (ICB) and continuing (CCB) calibration blanks were analyzed immediately after instrument calibration, after every 10 samples or more frequently, and at the conclusion of each analytical run, with the following exception: no CCV/CCB pair was analyzed at the conclusion of the ICP run. However, only interference check samples were analyzed after the final CCV/CCB pair, and data quality was not affected. Results for all CCVs fell within 90–110 percent of the expected value (80–120 percent for mercury), as required

by EPA CLP. Instrument calibration remained within control limits for all samples thorughout each sample run and for all other analytes.

Instrument-Specific Quality Control Procedures

ICP—A serial dilution sample is required by EPA CLP protocols to check for matrix interference in samples analyzed by ICP. All samples analyzed by ICP were diluted to one fifth of their initial concentration to bring manganese concentrations within the linear range of the ICP. The laboratory chose to report the results of diluted Sample 3 on CLP Form 9, *ICP Serial Dilutions*. A further serial dilution was required by CLP protocols to obtain a diluted result for manganese, but was not performed. Results of the serial dilution for iron, magnesium, nickel, and zinc were within the CLP control limit of 10-percent difference from the undiluted result. The results for aluminum and copper were not applicable because the undiluted concentration of these metals was not sufficiently high. The result for calcium (11-percent difference) exceeded control limits, with the diluted result (corrected for dilution) exceeding the undiluted result. All calcium data were qualified *E* by the laboratory and *J* during the quality assurance review. Reported calcium results may have a small negative bias of approximately 10 percent due to matrix interference.

Interference check samples (ICSs) were analyzed at the beginning and end of the ICP sample run to check for interference by other metals. Results met CLP control limits in all cases. To extend the linear range of the ICP to accommodate the high analyte concentrations present in the ICSs, a second calibration curve was obtained for some of the ICS analytes using higher standards than were used for the sample analyses. The analytical wavelength and all instrument parameters remained the same. Calibration was verified at the higher calibration curve as well.. Data relating to the higher calibration curve were labeled "secondary lines" in the original data.

GFAA—Quality control procedures for GFAA analyses included duplicate injection of all samples and analysis of a postdigestion analytical spike with each sample. Results of duplicate injections were spot-checked at a frequency of approximately 10 percent. All examined duplicate injection results agreed within 20-percent coefficient of variation, as required by CLP protocols.

Recoveries of the analytical spike for numerous samples and analytes did not meet CLP control limits of 85–115 percent. In most cases, these data were qualified *W* (analytical spike recovery did not meet control limits and sample absorbance is less than 50 percent of spike absorbance) by the laboratory, or MSA was used to analyze the samples as required by CLP protocols. Sample results obtained by MSA were qualified *S* by the laboratory if the correlation coefficient obtained with the MSA results was ≥0.995. Results qualified *S* are reliable and are not considered to be estimates. Sample results obtained by MSA with correlation coefficients <0.995 were qualified + by the laboratory and *J* during the quality assurance review. These results are estimates.

A systematic calculation error was made by the laboratory for all sample results obtained by MSA. The error consisted of the misassignment of axes to the sample concentration values and to the instrument response values, resulting in an incorrect value for the slope of the instrument response per added concentration and consequently for the analyte concentration in the sample. Results obtained with a poor correlation coefficient showed the greatest magnitude in the error. All results were corrected during quality assurance review.

Several errors were made by the laboratory in following the CLP sample analysis sequence for analyses by GFAA. The analytical spike recoveries of silver and lead in the first method blank (122- and 119-percent recovery, respectively) exceeded CLP control limits (85–115 percent). According to U.S. EPA (1987), the problems should have been corrected and acceptable results should have been generated for the method blank prior to sample analysis. A qualifier (*E*) was applied to the silver result for Sample 5 (the only result not obtained by MSA) by the laboratory because of the high analytical spike recovery from the blank, but was removed during the quality assurance review because data qualification is not automatically warranted in this case. All samples results for lead from the first digestion group were obtained by MSA and were not qualified by the laboratory or during the quality assurance review.

The matrix spike samples for lead and silver should have been analyzed by MSA because the analytical spike recoveries were low (74- and 58-percent recovery, respectively) for these analytes. The initial sample and duplicate (Sample 2) for silver were analyzed by MSA. The spike results for silver and lead are estimates.

The analytical spike recovery for lead in Sample 3 was 34 percent. This sample should have been diluted and reanalyzed (U.S. EPA 1987); however, MSA was performed instead. Samples 2 (duplicate), 5, and 6 were analyzed by MSA for arsenic and had correlation coefficients below the control limit. These samples should have been reanalyzed, but were not. The correlation coefficient for arsenic by MSA in Sample 2 (duplicate) was 0.909, well below the control limit of 0.995, and the curve generated by the standard additions was exponential in appearance. This result (45.5 µg/L) was rejected during the quality assurance review because of the poor correlation coefficient, and the initial result (26.2 µg/L) was accepted as an estimate.

Detection Limits

All reported instrument detection limits (IDLs) were below or equal to the CLP contract-required detection limits (CRDLs) (Table F-2). The IDL for lead by GFAA was omitted from CLP Form 11, but was subsequently provided by the laboratory. The IDLs reported for GFAA analytes were estimated by laboratory personnel based on their experience with the instrument and were not determined statistically as required by CLP protocols (U.S. EPA 1987). Data were not qualified for this omission. Based on the quality assurance

review of original laboratory data, in the reviewer's judgment the laboratory estimates of detection limits tended to be high. Use of statistically determined detection limits may result in lower values than the reported IDL in many cases.

Accuracy

The laboratory performed one LCS analysis (using a commercially available standard prepared specifically for CLP analyses) and one predigestion matrix spike analysis (Sample 1 for mercury, and Sample 2 for all other analytes). Recovery of all analytes except silver from the LCS ranged from 84 to 112 percent. Silver recovery was 52 percent (Table F-3). CLP control limits for metals in the LCS are 80- to 120-percent recovery (except for silver, which has no contractual control limit [U.S. EPA 1987]). All results for silver were qualified *J* during the quality assurance review because of the poor LCS recovery (U.S. EPA 1988).

Predigestion matrix spike recovery was within control limits (75–125 percent; U.S. EPA 1987) for all metals except cadmium, lead, mercury, and silver (Table F-4). Results for cadmium and lead (194- and 261-percent recovery, respectively) were greater than the control limit, and all sample results greater than the IDL were qualified *J* during the quality assurance review (U.S. EPA 1988). Only Sample 2 was not qualified for cadmium because none was detected. The spike results for both lead and cadmium are questionable because the matrix duplicate results for Sample 2 exceeded control limits, so a reliable sample concentration is not available. The spike sample result for lead is also questionable because the sample should have been analyzed by MSA, but was not. In addition, at least one method blank for lead was contaminated (as discussed in the *Blanks* section); nonsystematic lead contamination may also have contributed to the poor replicability of the duplicates and the high spike recovery for lead. All data were qualified as estimated despite the uncertainty in the matrix spike results because the magnitude of the control limit exceedance was large for both analytes.

All mercury data were qualified *J* during the quality assurance review because predigestion spike recoveries (40 and 39 percent, respectively) were much lower than control limits. Recovery for a postdigestion mercury spike analyzed for Sample 1 was 38 percent, similar to the predigestion spike result. This result indicates that a matrix interference at the spectrophotometer was probably responsible for poor recovery. Reported results for mercury may be lower than the actual sample concentrations.

The matrix spike result reported for silver was lower than the result reported for the unspiked sample. The analytical spike result of the matrix spike sample was low (58-percent recovery), and therefore the matrix spike sample should have been analyzed by MSA, but was not. The original and duplicate Sample 2 were both analyzed by MSA. The matrix spike result for silver was rejected during the quality assurance review. The matrix spike result for chromium was not applicable because the sample concentration exceeded 4 times the spike concentration. The magnitude of the precision error (the control limit is ≤20 relative percent difference [RPD]) may be significant with respect to

TABLE F-3. PERCENT RECOVERY FOR METALS IN LABORATORY CONTROL SAMPLE

Analyte	Percent Recovery[a]
Aluminum	98
Arsenic	105
Cadmium	112
Calcium	99
Chromium	109
Copper	101
Iron	99
Lead	98
Magnesium	99, 84, 93
Manganese	100
Mercury	111
Nickel	97
Silver	52
Zinc	98

[a] Percent recovery = $\frac{\text{measured value}}{\text{true value}} \times 100.$

TABLE F-4. MATRIX SPIKE RECOVERY FOR METALS IN SAMPLE 2

Analyte	Sample Result (µg/L)	Spike Added (µg/L)	Percent Recovery[a]
Aluminum	310	2,000	97
Arsenic	25	40	89
Cadmium	5 *U*[b]	5	194
Calcium	--	--	NR[c]
Chromium	69	10	NA[d]
Copper	27	250	103
Iron	7,090	1,000	77
Lead	29	20	261
Magnesium	--	--	NR
Manganese	6,560	500	76
Mercury[e]	0.2 *U*	1.0	40
Nickel	180	500	106
Silver	28 *R*[f]	10	--[f]
Zinc	180	500	95

[a] Percent recovery = $\frac{\text{spiked result} - \text{unspiked result}}{\text{spike added}} \times 100.$

[b] *U* - the analyte was not detected at the indicated concentration.

[c] A matrix spike was not required for this analyte (U.S. EPA 1987).

[d] The result is not applicable because the sample concentration is greater than 4 times the spike concentration.

[e] Sample 1 was spiked for mercury only.

[f] *R* - the spike sample result was rejected; the result is not meaningful.

the spike concentration in this situation, and spike recovery results cannot be clearly interpreted. Assessment of analytical accuracy was based on the LCS for both silver and chromium.

Precision

Duplicate subsamples of Sample 2 for all metals and Sample 1 for mercury only were analyzed by the laboratory. Results are summarized in Table F-5. All results except cadmium and lead were within the control limit of 25 RPD (for sample results >5 times the CRDL) or ± the CRDL (for results ≤5 times the CRDL) specified by the EPA. A qualifier (*) was applied to all cadmium and lead values by the laboratory or during the quality assurance review to indicate EPA CLP duplicate control limit exceedance, and all cadmium and lead values were qualified *J* during the quality assurance review.

The result for arsenic for Sample 2 (duplicate) as obtained by MSA and reported by the laboratory was rejected during the quality assurance review, but the result obtained initially by direct comparison to the instrument calibration curve was accepted as estimated (details in the *Calibration* section). The latter value was well within control limits, and the former value exceeded the control limit by less than 1 µg/L. The data qualifier (*) applied by the laboratory to the arsenic value for Sample 2 was removed during the quality assurance review. No arsenic data were qualified *J*.

Blanks

A method blank and several calibration blanks were analyzed with the samples for each metal. No contaminant was found in any method blank with one exception: lead was present (6.1 µg/L) in the method blank prepared with the second digestion batch. Results for Sample 2 and the duplicate and spike samples for Sample 2 were reported from this digestion batch. Sample 2 was qualified *U* (undetected at the reported concentration) during the quality assurance review because the sample result (29.4 µg/L) was <5 times the concentration in the method blank (U.S. EPA 1988). According to the laboratory worksheets for lead, the method blank prepared with the third digestion batch also contained lead (105 µg/L); however, data corresponding to this result were absent from the instrument printout, and the result was not entered onto the appropriate CLP form. The entry on the worksheet was apparently a transcription error, and no result is available for this method blank. The result reported for Sample 1 was obtained from this digestion batch and was qualified *J* during the quality assurance review.

Several results for CCBs exceeded the detection limits for calcium, manganese, and zinc. However, all associated sample results exceeded 5 times the concentration of the respective analyte found in any CCB, and were therefore not significant with respect to the expected analytical variability of sample results. No sample results were qualified as a result of detected analyte concentrations in associated CCBs.

TABLE F-5. DUPLICATE ANALYSIS RESULTS FOR METALS IN SAMPLE 2

Analyte	Sample Result (µg/L)	Duplicate Result (µg/L)	Control Limit[a]	Relative Percent Difference[b]
Aluminum	310	308	200	--
Arsenic	25	26	10	--
Cadmium	5 *U*[c]	17	5*[d]	--
Calcium	184,000	180,000	--	2
Chromium	69	78	--	--
Copper	27	29	15	--
Iron	7,100	6,700	--	8
Lead	29	47	--	46*
Magnesium	200,000	190,000	--	3
Manganese	6,600	6,400	--	2
Mercury[e]	0.2 *U*	0.2 *U*	0.2	--
Nickel	180	190	40	--
Silver	28	31	10	--
Zinc	180	190	--	3

[a] For results less than 5 times the CRDL, the difference between replicate sample results must be ≤ the CRDL.

[b] $RPD = \frac{|\ sample - duplicate\ |}{(sample + duplicate)/2}$.

[c] *U* - the analyte was not detected at the indicated concentration.

[d] Results followed by "*" exceed CLP control limits.

[e] Sample 1 was analyzed in duplicate for mercury only.

REFERENCES

U.S. EPA. 1987. U.S. EPA Contract Laboratory Program statement of work for inorganics analysis, multi-media, multi-concentration. SOW No. 788. U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA. 1988. Laboratory data validation: functional guidelines for evaluating inorganics analyses. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

QUALITY ASSURANCE REVIEW OF POLYCHLORINATED BIPHENYLS IN SEDIMENT

INTRODUCTION

This report documents the results of a quality assurance review of data for polychlorinated biphenyls (PCBs) in sediment samples as part of the sediment characterization of the Project Y site. The sampling and analysis plan (SAP) and the quality assurance project plan (QAPP) are described in the study proposal.

All laboratory analyses were performed by the laboratory in accordance with procedures specified in the SAP. Sample analyses were performed using modified versions of U.S. Environmental Protection Agency (EPA) SW-846 Method 8080 (U.S. EPA 1986); the modifications are detailed in the laboratory statement of work (SOW). Data validation was performed in accordance with the U.S. EPA (1988) functional guidelines for evaluating organic compound analyses, guidelines established in U.S. EPA (1986) SW-846 Method 8080, the data quality objectives specified in the SAP, and the requirements specified in the laboratory SOW.

The quality assurance review included examination and validation of the following data:

- Sample holding times and chain-of-custody records
- Initial and continuing calibration analyses, including calculations by least squares linear regression
- Reported detection limits
- Method blank analyses
- Matrix spike and matrix spike duplicate recoveries
- Surrogate compound recoveries
- All reported sample results, including verification of quantification, examination of chromatograms, and PCB identification.

OVERALL CASE ASSESSMENT

The results of the quality assurance review for the analysis of PCBs in the 64 sediment samples are presented below in two sections. These sections address completeness of the data package and the qualifiers assigned to individual measurements.

Summary of Completeness

A complete data package was submitted by the laboratory for 64 sediment samples, 4 method blanks, 4 matrix spikes, and 4 matrix spike duplicates. Data completeness is 100 percent of the total requested analyses; no results were rejected.

Summary of Data Qualifications

The results of analyses for PCBs in the 64 sediment samples associated with this project are acceptable for the intended purposes specified in the SAP. Some data were assigned a *J* qualifier to indicate that the values reported are estimates. The data are acceptable, but have a greater degree of uncertainty than nonqualified data.

A summary of the technical factors resulting in the qualification of the PCB data is as follows:

- The laboratory did not fully establish linearity for the initial calibration near the lower end of the standard curve. Demonstration of linearity near the lower end of the curve is important for validating to demonstrate the limits of detection and practical quantification limits specified in the laboratory SOW.
- The laboratory quantified all sample results using a single-point standard (i.e., the continuing calibration standard). However, quantification using a single-point standard is only acceptable if linearity is established throughout the calibration range in the initial calibration.
- The criterion for continuing calibration was not met for three of the eight total standard analyses.
- Surrogate recoveries for 13 samples did not meet quality control limits; the associated data were qualified as estimates.

In addition, all PCB values were recalculated because coeluting chromatographic peaks were used by the laboratory to identify PCBs; therefore, the peak heights used for quantification resulted in biased values. The recalculated values were typically one-half of the original concentrations reported by the laboratory. In addition, the laboratory occasionally incorrectly identified and reported results for specific PCBs. During the quality assurance review, these data were corrected.

A complete discussion of the results of the data validation and specific problems identified during the quality assurance review is provided below.

HOLDING TIMES

All storage conditions and sample holding times were properly met by the laboratory. The holding time requirements for PCB analyses specified in the SAP are as follows:

- All samples must be shipped on ice to the laboratory and stored at −18°C until sample extractions are performed
- Sample extracts must be analyzed within 40 days
- Sediment samples must be kept frozen and extracted within 6 months from the date and time of sample collection.

The 64 sediment samples were collected between _____ and _____; the samples were received at _____ on _____. Samples were extracted between _____ and _____, and the sample extracts were analyzed between _____ and _____.

ANALYTICAL METHODS

Samples were analyzed for PCBs using a modified version of U.S. EPA (1986) SW-846 Method 8080. The modifications are specified in the SAP and the laboratory SOW and include the following:

- Larger sample size for extraction (i.e., approximately 100 grams, wet weight)
- In addition to the Contract Laboratory Program (CLP) surrogate compound dibutylchlorendate (DBC), the use of an additional surrogate compound (4,4'-dibromooctafluorobiphenyl [DBOFB]) to monitor recovery on a sample-by-sample basis
- Sample extract cleanup procedures as required using alumina column chromatography by EPA Method 3610, florisil column chromatography by EPA Method 3620, and elemental sulfur cleanup by EPA Method 3660
- Megabore capillary gas chromatography/electron capture detection (GC/EC-D) analysis to enhance resolution and reduce potential interferences
- Use of a multipoint calibration for all Aroclor® mixtures and analysis of a check standard of 0.1 ng (on-column) for verification of instrument sensitivity to assess the validity of the required detection limits.

The laboratory generally performed the recommended modifications. Florisil column chromatography was used for a limited number of samples. EPA Method 3660 (mercury cleanup) and a sulfuric acid cleanup step were used to remove elemental sulfur; the sulfuric acid cleanup step was used on all samples associated with this project. The use of sulfuric acid was approved by the project manager during sample processing.

CALIBRATION

The results of all initial and continuing instrument calibrations performed by the laboratory are generally acceptable. Specific problems identified during this quality assurance review are discussed in the section below.

Instrument calibration is performed to establish and ensure that the chromatographic system is capable of producing acceptable and reliable analytical data. An initial calibration is performed prior to sample analysis to establish the linearity of the chromatographic system, including demonstrating that all target compounds can be detected. Continuing calibrations are performed to verify that instrument performance is stable and reproducible on a day-to-day basis. The initial and continuing calibrations are to be performed according to procedures established by CLP protocols and modified in the SAP and the laboratory SOW.

A detailed description of the results for initial and continuing calibrations is presented below.

Initial Calibration

The laboratory performed an initial three-point calibration using concentrations of 0.4, 1.0, and 5.0 ng (on-column) for the five Aroclor® mixtures (Aroclor® 1016, 1221, 1232, 1248, and 1260). A five-point initial calibration (0.4, 1.0, 2.0, 3.0, and 5.0 ng) was performed for PCB 1242 and PCB 1254.

Linearity of the initial calibration to zero concentration is assumed when the percent relative standard deviation (RSD) of the calibration factors is ≤20 percent over the entire calibration range (U.S. EPA 1986). Additionally, the correlation coefficients (r^2) generated by least squares linear regression should be greater than 0.9950 to demonstrate linearity.

The laboratory calculated the r^2 values for the initial calibrations using the sum of all chromatographic peaks that were integrated (i.e., from the first peak integrated, the injection peak, to the last peak integrated) to perform the calculations. Only the chromatographic peaks representative of a specific PCB mixture should be used for performing these calculations. Therefore, all standard chromatograms were reviewed during the quality assurance review and the r^2 values were recalculated.

The recalculated results generated using least squares linear regression indicate that linearity through the origin was not established. While linearity through the origin is not uncommon for this type of analysis, most PCB concentrations that were recalculated are in this low concentration range. Therefore, the results for PCBs were assigned a *J* qualifier to indicate estimated values.

Continuing Calibration

The number of continuing calibrations is acceptable; however, the frequency of calibrations is not acceptable. The data were not qualified for unacceptable frequency of antimony calibration because of the numerous other problems identified and discussed in other sections of this report.

The criteria for acceptable continuing calibration require that the calibration factors for all target compounds have a difference of ≤15 percent from the average calibration factor calculated for the associated initial calibration (U.S. EPA 1986). The 15-percent difference value is required for results calculated using the chromatographic column that is used for quantitative purposes. In addition, the percent difference of the calibration factors calculated for the chromatographic column used for confirmation must be ≤20 percent (U.S. EPA 1986). If the criteria for the percent differences are not met, then a new initial calibration sequence must be prepared.

The laboratory performed 8 continuing calibration analyses during the analysis of the 64 sediment samples. The criteria for continuing calibration were not met for three of eight calibrations performed (ranging from 32- to 92-percent difference). In addition, the laboratory typically performed continuing calibrations at the end of a given daily analytical sequence or the calibrations were clustered together.

METHOD BLANK ANALYSIS

Method blank analysis is performed to determine the extent of laboratory contamination of samples. The four method blank analyses for this project are acceptable; PCBs were not detected.

ACCURACY

Accuracy of the analytical results is expressed in terms of the bias and precision of measurements. Bias is assessed by evaluating the recoveries of the surrogate compounds and the matrix spike recoveries calculated for sample analyses. Precision is assessed by evaluating the differences between duplicate matrix spike analyses. These results are presented below.

Surrogate Compound Recoveries

The surrogate compound recoveries reported for the 64 sediment sample analyzed are acceptable, except 13 surrogate recoveries did not meet the quality control limits and the associated data are accepted as estimates. The data quality objective for acceptable recovery for surrogate recovery is 100±50 percent.

The recoveries for DBC ranged from 0 to 160 percent, with an average recovery of 70 percent. The recoveries for DBOFB ranged from 0 to 128 percent, with an average recovery of 71 percent. Thirteen surrogate recoveries exceeded the quality control limits; four recoveries were reported at zero percent, and nine recoveries were less than 50 percent but greater than zero percent. No data were rejected because only one unacceptable surrogate recovery was reported for a given sample and the other surrogate recovery value was acceptable. The values for PCBs reported in these samples were assigned a *J* qualifier to indicate the values are estimates.

Matrix Spike Recoveries

The results for the matrix spike recoveries are acceptable for the four sets of duplicate matrix spike analyses that were performed, except for three results that are acceptable as estimates. All matrix spike analyses were performed using Aroclor® 1254 and the samples chosen by the laboratory for the matrix spikes had detectable amounts of PCBs.

The criteria for acceptable matrix spike recovery is 100±50 percent. All recoveries were recalculated during the quality assurance review. The recalculated matrix spike recoveries ranged from 0 to 90 percent. Only three results did not meet the quality control limits. No data were rejected in accordance with procedures detailed by EPA CLP protocols (U.S. EPA 1988).

PRECISION

Two of the four total relative percent difference (RPD) values did not meet the quality control criteria for precision. Precision is expressed as the RPD between the recoveries of the matrix spike and the matrix spike duplicate analyses performed on a sample. The quality control criterion for precision is ±50 percent. The RPDs calculated from the duplicate matrix spike recoveries ranged from 13 to 90 percent.

IDENTIFICATION OF COMPOUNDS

All chromatograms were examined during the quality assurance review to verify that PCB identifications and confirmations (where applicable) are correct. The confirmation of the PCB identification during the quality assurance review focuses on false positives. However, PCBs reported as not detected are also evaluated to investigate the possibility of false negatives. Confirmation of possible false negatives is addressed by reviewing

other factors relating to analytical sensitivity (e.g., detection limits, instrument linearity, and analytical recovery).

Either Aroclor® 1254 or Aroclor® 1260, or a mixture of the two, was identified in 55 of 64 samples associated with this study. Absolute identification for the presence of Aroclors® 1254 or 1260 could not be confirmed during the quality assurance review because all chromatograms generated with the confirmational chromatographic column drifted off scale (i.e., 100 percent, full-scale deflection). Additional sample dilutions were not performed for these samples. Therefore, results generated using data obtained from only one chromatographic column were used to perform quantification and identify the PCBs. As a result, all results were assigned a *J* qualifier to indicate the values reported are estimates.

COMPOUND QUANTIFICATION AND REPORTED DETECTION LIMITS

All quantifications performed by the laboratory were corrected during the quality assurance review. The laboratory had not accounted for coeluting peaks when Aroclors® 1254 and 1260 were present in a given sample; the inclusion of coeluting peaks resulted in biased values. Quantification of the reported data and the reported detection limits were recalculated to ensure all results are accurate and consistent with the requirements established in U.S. EPA (1986) SW-846 Method 8080, the SAP, and the laboratory SOW.

During the quality assurance review, chromatographic peaks characteristic to each PCB mixture were chosen to check quantifications and their identity. The heights of selected integrated peaks for a specific PCB mixture used for calibration were summed to recalculate the r^2 values, and concentrations of PCBs detected in the samples were recalculated using least squares linear regression. The results for PCBs quantitated in the samples were typically one-half of the values originally reported by the laboratory; all results were assigned a *J* qualifier to indicate estimated values.

The laboratory reported limits of detection of 5 µg/kg (wet-weight basis) for Aroclors® 1016, 1254, and 1260 and 10 µg/kg (wet-weight basis) for Aroclors® 1221, 1232, 1242, and 1248 in most samples. Overall, the laboratory reported limits of detection that range from 5 to 100 µg/kg (all values are adjusted for dilutions that may have been performed).

REFERENCES

U.S. EPA. 1986. Test methods for evaluating solid waste (SW-846): physical/chemical methods. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA. 1988. Laboratory data validation: functional guidelines for evaluating organics analyses. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

APPENDIX G

Analytical/Environmental Laboratory Audit Standard Operating Procedure

CONTENTS

ANALYTICAL/ENVIRONMENTAL LABORATORY AUDIT STANDARD OPERATING PROCEDURE

1. PURPOSE AND INTRODUCTION

The purpose of this standard operating procedure (SOP) is to provide guidance to EZ Consultants (EZ) staff in auditing analytical or environmental testing laboratories. The audit requires evaluation of information collected during the review of laboratory documents, performance of site interviews, and observation of normal laboratory operations. Basic procedures for arranging and performing a site visit are provided, as well as a checklist for items to be considered during the audit process, and an evaluation guide. Portions of the audit checklist form (Attachment 1) are based upon laboratory evaluation checksheets developed by the U.S. EPA Industrial Technology Division.

There are two typical reasons why an audit is requested to be performed: to determine the capability of a laboratory to perform (future) testing for EZ; or to evaluate the quality of data submitted, usually on behalf of a third party. The SOP outlined below is applicable in both cases.

2. AUDITOR QUALIFICATIONS

The auditor should have the technical experience necessary to perform the audit, i.e., familiarity with the analytical methods of interest, instrumentation used, standard QA practices, and general good laboratory practices. The auditor should also be familiar with this SOP.

3. REQUEST FOR AUDIT

A staff member desiring a laboratory audit be performed can contact the EZ chemistry group and request an auditor be assigned for this task.

4. CLARIFICATION OF AUDIT OBJECTIVES

The auditor should consult the staff member requesting the audit to determine the purpose of the audit and the rigor with which the audit must be performed. The extent of the audit and the intensity of scrutiny will vary, according to the type of laboratory, analyses,

and type of project which are involved. The auditor should get clear direction from the individual requesting the audit to determine the intensity of review which is desired. Information necessary to make this decision include:

- Reason for audit
- Rigorousness of the data requirements
- Type of project for which data are (to be) collected
- Analytical methods required.

5. ESTIMATE OF AUDIT COSTS

The labor costs involved for the audit will depend on the intensity of the audit, which in turn depends upon factors such as the following:

- Type and size of project involved
- Type of laboratory involved
- Rigorousness of information requirements
- Required analytical methods
- Size and organization of the laboratory
- Accessibility of documents for review
- Type of audit report necessary.

For a rough estimate, the audit of a small, subcontract laboratory with 10 staff members, producing standard CLP data packages for inorganics, with all necessary documents available in the EZ contract files would take approximately 18 hours of the auditor's time: eight hours for audit preparation, four hours for the site visit (excluding travel), and six hours for evaluation and report generation. Additional labor costs would include clerical, word processing, and editing staff time. Other direct costs such as travel expenses and computer time would also need to be included.

6. PREPARATION FOR THE AUDIT

6.1 Identification of Laboratory Contact Person

If a laboratory (which will be) performing analyses for EZ is to be audited, then the auditor should contact the laboratory directly. Usually the best person with whom to establish contact is the technical director or lab manager, if such a position exists.

If the laboratory to be audited is (or will be) performing analyses for a third party, that party should first be contacted, and their assistance should be enlisted to establish contact with the laboratory.

6.2 Initial Discussion with Laboratory Management

Initiate preliminary discussions with the laboratory contact person to:

- Obtain a profile of laboratory, e.g., what types of samples and analyses are handled, what clients are served, what level and types of services are available, how lab is managed, identification of the managerial chain, management's overall philosophy of quality, type of quality program in place.
- Identify the primary concerns, e.g., potential or perceived problems, perceived strengths.
- Identify the expectations, e.g., reason for desiring an audit, expected use of the outcome.
- Identify any problems the laboratory may have with EZ.

If at all possible, do not take an adversarial attitude, but instead try to foster a cooperative relationship with the laboratory. This is especially important when there have been previous problems or concerns regarding the quality of data produced by the laboratory. It is much easier to obtain necessary information and to resolve problems if an open, cooperative relationship can be established for the audit process.

6.3 Pre-Site Visit Activities

- Review the audit checklist form (Attachment 1): determine what information will be necessary to complete the form and prepare for the site visit. The topics generally covered during the site visit include organization and personnel training, client requests, sample receipt and storage areas, sample preparation areas, general laboratory facilities, documents, standards, procedures, instrumentation, quality control, data review, data management, and report generation.
- Collect relevant information: gather applicable laboratory or project documents which will be helpful in filling out portions of the audit checklist in advance, or aid in completing the audit report. Such documents could include the laboratory statement of qualifications (SOQ), statement of work (SOW), contract or bid package, relevant analytical or sampling methods, EPA or state performance evaluations performed within the past year, and the laboratory QA/QC manual. If the laboratory is currently under contract with EZ, or a third party for whom EZ is performing the audit, obtain the applicable documents from our contract files or

from the third party. If the laboratory is being considered for performance of future work, obtain copies of the documents from the laboratory, if possible.

- Review the assembled information and begin filling out the audit checklist form following the instructions in Section 8. Make notes of additional questions regarding the laboratory which will need to be answered. Note that the audit checklist form (Attachment 1) contains general guidelines for laboratories testing hazardous materials, therefore, not all of the questions may be applicable. The audit procedure will proceed more quickly if those sections which are not applicable are marked with "N/A" in advance.

6.4 *Schedule of the Site Visit*

Remind the laboratory contact person of the purpose of the audit when you make the arrangements for a site visit. Since the most useful information can be gained while the laboratory is operating under typical conditions, only two to three days' advance warning should be allowed prior to the site visit. This should allow enough time for the laboratory to arrange that key individuals are available for site interviews.

It is helpful to the laboratory staff if the auditor provides the laboratory with information on the audit and explains how the site visit will be conducted. See Section 7 for a typical agenda for a site visit. Information which should be discussed in making arrangements for the site visit should include:

- Purpose of the audit (e.g., potential contract, resolution of problems)
- Estimate of time the site visit will take (typically, three to four hours for a small laboratory performing one type of analysis)
- Areas of the laboratory to be audited
- Topics to be covered during the site visit (e.g., organization and personnel training, client requests, sample receipt and storage areas, sample tracking, sample preparation areas, general laboratory facilities, documents, standards, procedures, instrumentation, quality control, data review, data management, and report generation)
- Staff requested to be available to the auditor during the site visit (e.g., lab manager or director, QA/QC officer, sample management supervisor, sample custodian, sample processing supervisor, inorganic and/or organic section supervisors, bench chemists and technicians, data management); there should be a specific laboratory staff member identified to provide information on each of the topics listed above

- Documents requested to be available to the auditor during the site visit (e.g., QA program documents, policies and procedures, manuals, control charts, corrective action reports)
- Proposed site visit schedule (see Section 7 for a typical schedule)
- Specific problems, if any.

7. PERFORMANCE OF THE SITE VISIT

It is important to perform the site visit in a professional, efficient manner, and to minimize disruption of the normal laboratory activities. Try to have a cooperative attitude, and emphasize that this site visit is an information gathering activity that may provide helpful information to their organization as well. Do not make critical remarks or point out flaws, but include such remarks in written notes. One way to conduct a site visit is as follows:

- Initial briefing: meet the key personnel (managers and supervisors) in the laboratory as a group and briefly explain the purpose of the audit. Have one of the laboratory staff present a general overview of the laboratory organization and capabilities, and introduce personnel. Ask that a history be presented on a sample, beginning with the initial request for analysis, receipt of the sample from the client, through internal procedures and analysis, generation of data and submittal of the final data report to the client. Set the format for this initial briefing with the laboratory contact person prior to the site visit. Try to arrange to keep this initial briefing to approximately half an hour.
- Document review: have arrangements made ahead of time for an opportunity to review the laboratory documents you requested be available. This can be done at this point, during the interview, or near the end of the interview, just prior to the final briefing.
- Observation of the various areas of the laboratory: make arrangements ahead of time with the laboratory contact person to visit each area of interest in the laboratory to make observations. Cover each of the applicable topics on the audit checklist. Follow the sample history, as presented earlier by the laboratory. The audit checklist is organized to facilitate this task.
- Information gathering: collect information on the audit checklist as the site visit progresses. Make checks in the appropriate places, or write in the information necessary for each question as responses are given. It is difficult to remember all the information provided, and is important to be as accurate as possible in recording responses at the time they are provided.

If possible, arrange to speak with bench level technicians and analysts during the observation process. Specific instructions for filling out the audit checklist are provided in Section 8.

- Final briefing: meet with the key personnel, or at a minimum with the laboratory director or QA manager, at the end of the interviews to ask any questions which may not have been answered. If additional information is necessary, ask that it be forwarded. Since it is not possible to tell the laboratory at this time whether the audit was passed or not, because a detailed review of the information provided on the checklist will be required, make no comment on whether the laboratory has passed the audit. However, give an indication of when the laboratory may expect an audit report, and to whom this report will be made available. Always thank the laboratory staff for their time and for allowing you to disrupt their schedules.

8. USE OF THE AUDIT CHECKLIST FORM

The audit checklist form (Attachment 1) provides general guideline questions for laboratories performing hazardous materials analysis. The EZ chemistry group leader should be consulted by the auditor, if it is felt that a project-specific form must be generated.

The checklist is divided into several sections:

- Organization and Personnel
- Sample Receipt and Storage Area
- Sample Preparation Area/Facilities
- Instrumentation
- Quality Control
- Data Handling and Review
- QC Manual Checklist
- Summary.

It is assumed that appropriate staff (who have been previously identified) will be made available to the auditor to answer the questions in each of these sections. Make checks in the appropriate boxes, or write in the information necessary for each question as the answers are provided. Do not make critical remarks or point out flaws, but include such information in written notes. Either write all notes on the checklist form or attach notes to the form. Ask to inspect documents, when appropriate, to verify answers.

9. USE OF THE AUDIT SCORING GUIDELINES

Once the site visit has been completed and any additional information has been provided to the auditor, the evaluation of the laboratory can be completed.

Point distributions for each response which can be answered "yes" or "no" are given in the scoring guideline in Attachment 2. In some cases, it may be necessary to check both, as not all requirements may be fulfilled. All points are then totaled and the percentage of the maximum possible points is then calculated. Questions which are not applicable to a particular facility are not scored, and are not counted toward the maximum possible points, thereby neither rewarding or penalizing the laboratory. Responses to questions which have no point value will be used to determine marginal cases of pass or fail. The following criteria are given for acceptability or nonacceptability:

86–100% of maximum possible points	=	acceptable audit
76–85% of maximum possible points	=	provisionally acceptable audit (based on responses to nonpoint questions)
below 76% of maximum possible points	=	unacceptable audit

10. AUDIT REPORT

An internal memo summarizing the results should be provided to the EZ staff who requested the audit be performed. In many cases, the third party may wish to receive copies of the completed audit report for their records. An example memo is provided as Attachment 3 of this procedure. If it has been requested, a copy should also be provided to the audited laboratory.

Attachment 1

ANALYTICAL CHEMISTRY LABORATORY AUDIT GUIDELINES

Laboratory: _____ Date: _____

Address: _____ Telephone: _____

_____

Auditor(s): _____

_____

Laboratory Personnel Interviewed:

Name	Title

Laboratory Accreditation/Certification:

		Expiration	

Comments:

_____

_____

_____

Score:

	Yes	No	Points	Comments
A. Organization and Personnel				
1. Is there an organizational chart available?	___	___	___	
2. Is everyone in the organization familiar with it?	___	___	___	
3. Is an up-to-date file maintained in the laboratory describing the educational background and/or related work experience of all laboratory personnel?	___	___	___	
4. Is there a formal training program for personnel?	___	___	___	
5. Are employees required to demonstrate proficiency with analytical instrument operation, methods, or techniques prior to working on client samples?	___	___	___	
6. Is this proficiency testing documented?	___	___	___	
7. Is the organization adequately staffed to meet commitments in a timely manner?	___	___	___	
8. Is there a designated QA/QC Officer?	___	___	___	
9. To whom does the lab QA/QC Officer report? _____				
10. Was the lab QA/QC Officer available during the audit?	___	___	___	
11. Was a program manager or laboratory manager available during the evaluation?	___	___	___	

Comments: _____

_____

_____

B. Sample Receipt and Storage Area				
1. Is a sample custodian designated?	___	___	___	
2. Are the responsibilities clearly defined?	___	___	___	
In writing?	___	___	___	
3. Is there a standard sample login procedure followed?	___	___	___	
4. Does the procedure include adequate inspection of samples and accompanying documents to verify that they are intact, complete, and consistent?	___	___	___	
5. Is there an inspection checklist?	___	___	___	
6. Does it document adequately the nature and condition of samples and documentation?	___	___	___	
7. Is the integrity of samples and shipping containers being documented?	___	___	___	

		Yes	No	Points	Comments
8.	Are samples logged into a bound notebook?	___	___	___	
	a. Computerized lab management system?	___	___	___	
	b. Other? (describe: _____)	___	___	___	
9.	Does the login record document:				
	a. Field and laboratory ID	___	___	___	
	b. Analyses requested	___	___	___	
	c. Storage location	___	___	___	
	d. Signature of custodian	___	___	___	
	e. Collection date	___	___	___	
	f. Receipt date	___	___	___	
	g. Analysis due date	___	___	___	
	h. Sample holding time	___	___	___	
	i. Special instructions	___	___	___	
10.	Is there a daily summary of information such as samples received, analyses requested, date sampled, or date received?	___	___	___	
11.	To whom is this summary distributed? _____				
12.	Are login records filed and readily retrievable?	___	___	___	
13.	How far back in time can records be retrieved? _____				
14.	Are written SOPs developed for receipt and storage of samples?	___	___	___	
15.	Are they available to and understood by laboratory personnel?	___	___	___	
16.	Is a clean area available for receiving and opening sample shipments?	___	___	___	
17.	Is this area separated from other lab operations (consider not only spatial separations, but air flow, personnel, traffic, etc.)?	___	___	___	
18.	Does the custodian understand the importance of preventing lab contamination?	___	___	___	
19.	If appropriate, are the pHs of samples measured and recorded to verify that they are preserved?	___	___	___	
20.	What percentage of samples is checked? _____				
21.	Are records of these checks retained?	___	___	___	
22.	Are facilities adequate for the storage of samples?	___	___	___	
23.	Are samples stored so as to maintain their preservation?	___	___	___	

	Yes	No	Points	Comments
24. Are volatile samples stored separately from semivolatile samples?	___	___	___	
25. Is the temperature of the cold storage area recorded daily?	___	___	___	
a. Are excursions noted, along with descriptions of corrective action taken?	___	___	___	
b. Is this being reviewed periodically by a supervisor or the QC unit?	___	___	___	
26. Is the sample storage area secure?	___	___	___	

27. How is sample identification maintained?

_____
_____
_____

28. Is positive sample chain-of-custody maintained within the lab? ___ ___ ___

29. How are samples tracked through the lab?

_____
_____
_____

30. How long are samples retained? _____

Sample extracts? _____

31. How are special instructions regarding preparation, analysis, or turnaround times transmitted within the laboratory?

_____
_____

Comments: _____
_____
_____

C. Sample Preparation Area/Facilities

1. Is the laboratory maintained in a clean and organized manner?	___	___	___	
2. Does the lab appear to have adequate work space (120 ft^2 per analyst)?	___	___	___	
3. Are the toxic chemical handling areas either stainless steel benches or an impervious material covered with absorbent paper?	___	___	___	
4. Are contamination-free work areas provided for the handling of toxic materials?	___	___	___	

		Yes	No	Points	Comments
5.	Are adequate exhaust hoods available to prevent contamination of personnel and the laboratory facility?	___	___	___	
6.	Are the flow rates and/or face velocities of these hoods periodically checked and recorded?	___	___	___	
7.	How frequently are they checked? ___				
8.	Are the procedures and records adequate to demonstrate the proper face velocity profile for each hood over the period of record?	___	___	___	
9.	Is the near-face interior of each hood clear of objects that might interfere with the proper face velocity profile and thereby reduce hood efficiency?	___	___	___	
10.	Are chemical waste disposal policies/procedures well-defined and followed by the laboratory?	___	___	___	
11.	Are records of waste containerization and disposal (lab logs, manifest, etc.) filed and retrievable?	___	___	___	
12.	Are voltage control devices installed on major instrumentation?	___	___	___	
13.	What is the laboratory's source of distilled/deionized water? ___				
14.	Is the conductivity of this water checked daily and data recorded (acceptable conductivity is 2:0–5.0 µmhos/cm at 25°C)?	___	___	___	
15.	Is the analytical balance located away from draft and areas subject to rapid temperature fluctuations?	___	___	___	
16.	Is it protected from vibration associated with activities in the facility (i.e., it should be on a heavy table, on a floor that does not bounce when walked on, etc.)?	___	___	___	
17.	Is the balance maintained by a certified technician?	___	___	___	
18.	Is the balance routinely calibrated with Class S weights and are the calibration data recorded?	___	___	___	
19.	Are the Class S weights handled properly to prevent contamination/damage?	___	___	___	
20.	How often are the Class S weights certified? ___				
21.	Are pH and ion selective meters properly calibrated and maintained; and are these activities recorded?	___	___	___	
22.	Are laboratory thermometers (including mercury-in-glass) calibrated at least yearly against an NIST traceable thermometer and documented?	___	___	___	

	Yes	No	Points	Comments
23. Are reagents dated upon receipt by labeling each container with the date received?	___	___	_____	
24. Is there a complete log of reagent and solvent supply giving the quantity, batch number, receipt date, percent activity, or purity?	___	___	_____	
25. Are reagents and standards checked prior to use?	___	___	_____	
26. Are solvent lots checked and documented prior to use?	___	___	_____	
27. Are reference materials properly labeled?	___	___	_____	
28. Is each spiking/calibration standard completely traceable to documented neat material or a documented purchased standard?	___	___	_____	
29. Is each logbook entry signed and dated by the individual who prepared the solution?	___	___	_____	
30. Are logbooks periodically reviewed and signed by a manager/supervisor?	___	___	_____	
31. Are logbooks maintained in a manner which allows complete traceability?	___	___	_____	
32. Are standards stored separately from samples and sample extracts?	___	___	_____	
33. Are volatile and semivolatile standard compounds properly segregated?	___	___	_____	
34. Are SOPs readily available to laboratory personnel?	___	___	_____	
35. Are glassware cleaning procedures documented?	___	___	_____	
36. Are the cleaning procedures consistent with EPA recommended procedures?	___	___	_____	
37. Is the temperature of the drying ovens recorded daily?	___	___	_____	
38. Is cleaned glassware properly handled and stored to prevent contamination?	___	___	_____	
39. How do lab personnel recognize glassware that has been prepared for specific function (e.g., organic vs. inorganic)? _____				
40. Is the laboratory secured?	___	___	_____	

Comments: _____

D. Instrumentation

1. Are instrument operating manuals available?	___	___	_____	

	Yes	No	Points	Comments
2. Do the operators demonstrate a good familiarity with the manuals?	___	___	_____	
3. Are there service contracts on the instrumentation (and is a record maintained of the service)?	___	___	_____	
4. Are in-house replacement parts available?	___	___	_____	
5. Have the instruments been modified in any way?	___	___	_____	
Describe the modifications and discuss ramifications: _____				
6. Are instruments properly vented or are appropriate traps in place?	___	___	_____	
7. Is a logbook maintained for each instrument?	___	___	_____	
8. Is a complete list of laboratory instrumentation available?	___	___	_____	
9. Are all calibration data hard-copied and retained?	___	___	_____	
10. When calibrating an AA:				
a. How many standards are run to generate the calibration curve?_____				
b. Is a new curve generated for each run?	___	___	_____	
c. Is a standard blank always run?	___	___	_____	
d. Is calibration checked immediately after completing as well as periodically throughout the run?	___	___	_____	
11. When calibrating an ICP:				
a. How many standards are run to generate the calibration curve?_____				
b. Is a new curve generated for each run?	___	___	_____	
c. Is a standard blank always run?	___	___	_____	
d. Is calibration checked immediately after completing as well as periodically throughout the run?	___	___	_____	
12. When calibrating a GC:				
a. How many standards are run to generate the calibration curve?_____				
b. Is a calibration check standard run daily?	___	___	_____	
c. What are the performance criteria for this standard?_____				
d. Is the instrument typically calibrated for every compound of interest?	___	___	_____	

	Yes	No	Points	Comments

e. How are retention times monitored for each compound of interest, and when is corrective action taken? _____

_____

_____

13. When calibrating a GC/MS:

a. How many standards are run to generate the calibration curve? _____

b. Is a calibration check standard run daily? ___ ___ _____

c. What are the performance criteria for this standard? _____

d. Is the instrument typically calibrated for every compound of interest? ___ ___ _____

e. Is the instrument tuned at least daily? ___ ___ _____

f. Do the tuning procedures conform to the methods for which the instrument is being used? ___ ___ _____

g. What compound and performance criteria are used? _____

h. Are surrogates and internal standards used? ___ ___ _____

i. Are surrogate and internal standard recoveries monitored? ___ ___ _____

j. What are the action limits? _____

_____

Comments: _____

_____

_____

E. Quality Control

1. Are method blanks prepared and analyzed with each batch of samples, for each analytical procedure, or some percentage? ___ ___ _____

What percentage:

a. For GC/MS analyses? _____
b. For GC analyses? _____
c. For AA/ICP analyses? _____
d. For wet chemistry? _____

2. At what frequency are lab duplicates prepared and analyzed:

a. For GC/MS analyses? _____
b. For GC analyses? _____
c. For AA/ICP analyses? _____

	Yes	No	Points	Comments
d. For wet chemistry? _____				
3. How are duplicate sample results tracked and used:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
4. At what frequency are lab spikes (e.g., spiked deionized water or clean soil) prepared and analyzed:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
5. At what stage of processing are samples spiked:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
6. Are matrix spiked samples employed:				
a. For GC/MS analyses?	___	___	_____	
b. For GC analyses?	___	___	_____	
c. For AA/ICP analyses?	___	___	_____	
d. For wet chemistry?	___	___	_____	
7. What action is taken when results exceed control limits:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
8. Are surrogate compounds utilized for GC/MS analyses?	___	___	_____	
9. When are the surrogates added to the samples? _____				
10. How many surrogate compounds are introduced? _____				
11. Is the percent recovery for each surrogate calculated?	___	___	_____	
12. Are those data reported?	___	___	_____	
13. Are performance criteria established for surrogates?	___	___	_____	
14. Are percent recoveries plotted on control charts?	___	___	_____	

	Yes	No	Points	Comments
15. What action is taken when results exceed limits? _____				
16. Are surrogate compounds utilized for GC analyses?	___	___	_____	
17. When are the surrogates added to the samples? _____				
18. How many surrogate compounds are introduced? _____				
19. Is the percent recovery for each surrogate calculated?	___	___	_____	
20. Are those data reported?	___	___	_____	
21. Are performance criteria established for surrogates?	___	___	_____	
22. Are percent recoveries plotted on control charts?	___	___	_____	
23. What action is taken when results exceed limits? _____				
F. Data Handling and Review				
1. Are computer programs validated prior to use?	___	___	_____	
2. Are records of the validation maintained?	___	___	_____	
3. Are user instructions complete and available to all users?	___	___	_____	
4. Do analysts/technicians record data in a neat and accurate manner?	___	___	_____	
5. Are all handwritten data recorded in nonerasable ink?	___	___	_____	
6. Have entries been obliterated (e.g., through cross-outs or "whiteout")?	___	___	_____	
7. Are data calculations spot-checked by a second person?	___	___	_____	
What percentage? _____				
8. Are these checks documented on the hard-copy data record, and dated and initialed by the reviewer?	___	___	_____	
9. Are raw data being identified with client name, project number, date, and other pertinent tracking information?	___	___	_____	
10. Are raw data (notebooks, data sheets, computer files, strip chart recordings) being retained for 5 years?	___	___	_____	
11. Is there a system for report, record, or data retrieval?	___	___	_____	
12. Do supervisory personnel review the data or QC results?	___	___	_____	
What percentage? _____				

	Yes	No	Points	Comments
13. Are these reviews documented?	___	___	___	
14. Are in-house QC charts maintained and available for onsite inspection for:				
a. Matrix spikes?	___	___	___	
b. Laboratory duplicates?	___	___	___	
c. Surrogate recoveries?	___	___	___	
d. Calibration check standards?	___	___	___	
15. Have method detection limit studies been performed for each method in use?	___	___	___	
a. How recently? ___				
b. Any procedural or configurational changes since then?	___	___	___	
16. Do records indicate that appropriate corrective action has been taken when analytical results fail to meet the QC criteria?	___	___	___	

Comments: ___

G. QC Manual Checklist

1. Does the laboratory have a QC manual?	___	___	___	
2. Does the manual address the following:				
a. Personnel?	___	___	___	
b. Facilities or equipment?	___	___	___	
c. Operation of instruments?	___	___	___	
d. Method validation	___	___	___	
e. Calibration frequency	___	___	___	
f. Standards preparation	___	___	___	
g. Documentation of procedures	___	___	___	
h. Preventive maintenance	___	___	___	
i. Reliability of data	___	___	___	
j. Data validation	___	___	___	
k. Feedback and corrective action	___	___	___	
l. Record-keeping	___	___	___	
m. Internal audits	___	___	___	

Comments: ___

	Yes	No	Points	Comments
H. Summary				
1. Do responses to the evaluation indicate that laboratory personnel are aware of QA/QC and its potential impact on the data?	___	___	_____	
2. Is a positive emphasis placed on QA/QC by laboratory management?	___	___	_____	
3. Have the responses been open and direct?	___	___	_____	
4. Has the attitude been cooperative?	___	___	_____	
5. Is the proper emphasis placed on quality assurance?	___	___	_____	

Comments: _____

Attachment 2

ANALYTICAL AUDIT SCORING GUIDELINES

Point distributions for each response that can be answered "yes" or "no" are given in the following guideline. In cases of incomplete fulfillment of requirements, both responses may be checked. All points are then totaled and the percentage of the maximum possible points is then calculated. Questions that are not applicable to a particular facility are not scored, and are not counted toward the maximum possible points, thereby neither rewarding nor penalizing the laboratory. Responses to questions which have no point value will be used to determine marginal cases of pass or fail. The following criteria are given for acceptability or nonacceptability:

86–100% of maximum possible points	=	acceptable audit
76–85% of maximum possible points	=	provisionally acceptable audit (based on responses to nonpoint questions)
below 76% of maximum possible points	=	unacceptable audit

		Yes	No	Comments
A.	**Organization and Personnel**			
1.	Is there an organizational chart available?	1	–1	
2.	Is everyone in the organization familiar with it?	1	–1	
3.	Is an up-to-date file maintained in the laboratory describing the educational background and/or related work experience of all laboratory personnel?	1	–1	
4.	Is there a formal training program for personnel?	1	–2	
5.	Are employees required to demonstrate proficiency with analytical instrument operation, methods, or techniques prior to working on client samples?	2	–2	
6.	Is this proficiency testing documented?	2	–1	
7.	Is the organization adequately staffed to meet commitments in a timely manner?	5	–1	
8.	Is there a designated QA/QC Officer?	2	–1	
9.	To whom does the lab QA/QC Officer report? _____			
10.	Was the lab QA/QC Officer available during the audit?	1	–1	
11.	Was a program manager or laboratory manager available during the evaluation?	1	–1	

Comments: _____

_____

_____

B.	**Sample Receipt and Storage Area**			
1.	Is a sample custodian designated?	2	–1	
2.	Are the responsibilities clearly defined?	1	–1	
	In writing?	1	–1	
3.	Is there a standard sample login procedure followed?	1	–1	
4.	Does the procedure include adequate inspection of samples and accompanying documents to verify that they are intact, complete, and consistent?	2	–1	
5.	Is there an inspection checklist?	1	–1	
6.	Does it document adequately the nature and condition of samples and documentation?	1	–1	
7.	Is the integrity of samples and shipping containers being documented?	1	–1	
8.	Are samples logged into a bound notebook?	5	–2	
	a. Computerized lab management system?	5	–2	
	b. Other? (describe: _____)	5	–2	

		Yes	No	Comments
9.	Does the login record document:			
	a. Field and laboratory ID	2	–2	
	b. Analyses requested	2	–2	
	c. Storage location	2	–2	
	d. Signature of custodian	2	–2	
	e. Collection date	2	–2	
	f. Receipt date	2	–2	
	g. Analysis due date	2	–2	
	h. Sample holding time	2	–2	
	i. Special instructions	2	–2	
10.	Is there a daily summary of information such as samples received, analyses requested, date sampled, or date received?	2	–2	
11.	To whom is this summary distributed? _____			
12.	Are login records filed and readily retrievable?	2	–2	
13.	How far back in time can records be retrieved? _____			
14.	Are written SOPs developed for receipt and storage of samples?	2	–1	
15.	Are they available to and understood by laboratory personnel?	1	–1	
16.	Is a clean area available for receiving and opening sample shipments?	1	–1	
17.	Is this area separated from other lab operations (consider not only spatial separations, but air flow, personnel, traffic, etc.)?	1	–1	
18.	Does the custodian understand the importance of preventing lab contamination?	1	–1	
19.	If appropriate, are the pHs of samples measured and recorded to verify that they are preserved?	1	–1	
20.	What percentage of samples is checked? _____			
21.	Are records of these checks retained?	1	–1	
22.	Are facilities adequate for the storage of samples?	1	–1	
23.	Are samples stored so as to maintain their preservation?	2	–1	
24.	Are volatile samples stored separately from semivolatile samples?	5	–2	
25.	Is the temperature of the cold storage area recorded daily?	2	–1	

		Yes	No	Comments
a.	Are excursions noted, along with descriptions of corrective action taken?	2	–1	
b.	Is this being reviewed periodically by a supervisor or the QC unit?	2	–1	
26.	Is the sample storage area secure?	1	–1	
27.	How is sample identification maintained?	1	–1	
28.	Is positive sample chain-of-custody maintained within the lab?	1	–1	
29.	How are samples tracked through the lab?			
30.	How long are samples retained? _____ Sample extracts? _____			
31.	How are special instructions regarding preparation, analysis, or turnaround times transmitted within the laboratory?			

Comments: _____

C. Sample Preparation Area/Facilities

1.	Is the laboratory maintained in a clean and organized manner?	2	–2	
2.	Does the lab appear to have adequate work space (120 ft^2 per analyst)?	1	–1	
3.	Are the toxic chemical handling areas either stainless steel benches or an impervious material covered with absorbent paper?	1	–1	
4.	Are contamination-free work areas provided for the handling of toxic materials?	1	–1	
5.	Are adequate exhaust hoods available to prevent contamination of personnel and the laboratory facility?	2	–1	
6.	Are the flow rates and/or face velocities of these hoods periodically checked and recorded?	1	–1	

		Yes	No	Comments
7.	How frequently are they checked? _____			
8.	Are the procedures and records adequate to demonstrate the proper face velocity profile for each hood over the period of record?	1	–1	
9.	Is the near-face interior of each hood clear of objects that might interfere with the proper face velocity profile and thereby reduce hood efficiency?	1	–1	
10.	Are chemical waste disposal policies/procedures well-defined and followed by the laboratory?	1	–1	
11.	Are records of waste containerization and disposal (lab logs, manifest, etc.) filed and retrievable?	1	–1	
12.	Are voltage control devices installed on major instrumentation?	1	–1	
13.	What is the laboratory's source of distilled/deionized water? _____			
14.	Is the conductivity of this water checked daily and data recorded (acceptable conductivity is 2.0–5.0 µmhos/cm at 25°C)?	2	–2	
15.	Is the analytical balance located away from draft and areas subject to rapid temperature fluctuations?	1	–1	
16.	Is it protected from vibration associated with activities in the facility (i.e., it should be on a heavy table, on a floor that does not bounce when walked on, etc.)?	1	–1	
17.	Is the balance maintained by a certified technician?	2	–2	
18.	Is the balance routinely calibrated with Class S weights and are the calibration data recorded?	2	–2	
19.	Are the Class S weights handled properly to prevent contamination/damage?	2	–2	
20.	How often are the Class S weights certified? _____			
21.	Are pH and ion selective meters properly calibrated and maintained; and are these activities recorded?	1	–1	
22.	Are laboratory thermometers (including mercury-in-glass) calibrated at least yearly against an NIST traceable thermometer and documented?	1	–1	
23.	Are reagents dated upon receipt by labeling each container with the date received?	1	–1	

		Yes	No	Comments
24.	Is there a complete log of reagent and solvent supply giving the quantity, batch number, receipt date, percent activity, or purity?	1	–1	
25.	Are reagents and standards checked prior to use?	1	–1	
26.	Are solvent lots checked and documented prior to use?	1	–1	
27.	Are reference materials properly labeled?	1	–1	
28.	Is each spiking/calibration standard completely traceable to documented neat material or a documented purchased standard?	2	–1	
29.	Is each logbook entry signed and dated by the individual who prepared the solution?	1	–1	
30.	Are logbooks periodically reviewed and signed by a manager/supervisor?	1	–1	
31.	Are logbooks maintained in a manner which allows complete traceability?	2	–2	
32.	Are standards stored separately from samples and sample extracts?	1	–1	
33.	Are volatile and semivolatile standard compounds properly segregated?	1	–1	
34.	Are SOPs readily available to laboratory personnel?	1	–1	
35.	Are glassware cleaning procedures documented?	2	–2	
36.	Are the cleaning procedures consistent with EPA recommended procedures?	5	–2	
37.	Is the temperature of the drying ovens recorded daily?	1	–1	
38.	Is cleaned glassware properly handled and stored to prevent contamination?	2	–2	
39.	How do lab personnel recognize glassware that has been prepared for specific function (e.g., organic vs. inorganic)? _____			
40.	Is the laboratory secured?	1	–1	

Comments: _____

D. Instrumentation

1.	Are instrument operating manuals available?	1	–1	
2.	Do the operators demonstrate a good familiarity with the manuals?	1	–1	

		Yes	No	Comments
3.	Are there service contracts on the instrumentation (and is a record maintained of the service)?	1	–1	
4.	Are in-house replacement parts available?	1	–1	
5.	Have the instruments been modified in any way?	–1	1	
	Describe the modifications and discuss ramifications: _____			
6.	Are instruments properly vented or are appropriate traps in place?	1	–1	
7.	Is a logbook maintained for each instrument?	1	–1	
8.	Is a complete list of laboratory instrumentation available?	1	–1	
9.	Are all calibration data hard-copied and retained?	5	–2	
10.	When calibrating an AA:			
	a. How many standards are run to generate the calibration curve? _____			
	b. Is a new curve generated for each run?	5	–2	
	c. Is a standard blank always run?	5	–2	
	d. Is calibration checked immediately after completing as well as periodically throughout the run?	5	–2	
11.	When calibrating an ICP:			
	a. How many standards are run to generate the calibration curve? _____			
	b. Is a new curve generated for each run?	5	–2	
	c. Is a standard blank always run?	5	–2	
	d. Is calibration checked immediately after completing as well as periodically throughout the run?	5	–2	
12.	When calibrating a GC:			
	a. How many standards are run to generate the calibration curve? _____			
	b. Is a calibration check standard run daily?	5	–2	
	c. What are the performance criteria for this standard? _____			
	d. Is the instrument typically calibrated for every compound of interest?	5	–2	

	Yes	No	Comments
e. How are retention times monitored for each compound of interest, and when is corrective action taken? _____			
13. When calibrating a GC/MS:			
a. How many standards are run to generate the calibration curve? _____			
b. Is a calibration check standard run daily?	5	–2	
c. What are the performance criteria for this standard? _____			
d. Is the instrument typically calibrated for every compound of interest?	5	–2	
e. Is the instrument tuned at least daily?	5	–2	
f. Do the tuning procedures conform to the methods for which the instrument is being used?	5	–2	
g. What compound and performance criteria are used? _____			
h. Are surrogates and internal standards used?	5	–2	
i. Are surrogate and internal standard recoveries monitored?	5	–2	
j. What are the action limits? _____			

Comments: _____

E. Quality Control

1. Are method blanks prepared and analyzed with each batch of samples, for each analytical procedure, or some percentage?	5	–2	
What percentage:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
2. At what frequency are lab duplicates prepared and analyzed:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			

	Yes	No	Comments
d. For wet chemistry? _____			
3. How are duplicate sample results tracked and used:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
4. At what frequency are lab spikes (e.g., spiked deionized water or clean soil) prepared and analyzed:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
5. At what stage of processing are samples spiked:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
6. Are matrix spiked samples employed:			
a. For GC/MS analyses?	1	–1	
b. For GC analyses?	1	–1	
c. For AA/ICP analyses?	1	–1	
d. For wet chemistry?	1	–1	
7. What action is taken when results exceed control limits:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
8. Are surrogate compounds utilized for GC/MS analyses?	5	–2	
9. When are the surrogates added to the samples? _____			
10. How many surrogate compounds are introduced? _____			
11. Is the percent recovery for each surrogate calculated?	5	–2	
12. Are those data reported?	2	–2	
13. Are performance criteria established for surrogates?	2	–2	
14. Are percent recoveries plotted on control charts?	2	–2	

		Yes	No	Comments
15.	What action is taken when results exceed limits? _____			
16.	Are surrogate compounds utilized for GC analyses?	1	–1	
17.	When are the surrogates added to the samples? _____			
18.	How many surrogate compounds are introduced? _____			
19.	Is the percent recovery for each surrogate calculated?	1	–1	
20.	Are those data reported?	1	–1	
21.	Are performance criteria established for surrogates?	1	–1	
22.	Are percent recoveries plotted on control charts?	1	–1	
23.	What action is taken when results exceed limits? _____			
F.	**Data Handling and Review**			
1.	Are computer programs validated prior to use?	2	–1	
2.	Are records of the validation maintained?	2	–1	
3.	Are user instructions complete and available to all users?	2	–1	
4.	Do analysts/technicians record data in a neat and accurate manner?	2	–1	
5.	Are all handwritten data recorded in nonerasable ink?	2	–2	
6.	Have entries been obliterated (e.g., through cross-outs or "whiteout")?	–2	2	
7.	Are data calculations spot-checked by a second person?	2	–2	
	What percentage? _____			
8.	Are these checks documented on the hard-copy data record, and dated and initialed by the reviewer?	2	–2	
9.	Are raw data being identified with client name, project number, date, and other pertinent tracking information?	2	–2	
10.	Are raw data (notebooks, data sheets, computer files, strip chart recordings) being retained for 5 years?	2	–2	
11.	Is there a system for report, record, or data retrieval?	2	–1	
12.	Do supervisory personnel review the data or QC results?	2	–1	
	What percentage? _____			
13.	Are these reviews documented?	2	–1	

	Yes	No	Comments
14. Are in-house QC charts maintained and available for onsite inspection for:			
a. Matrix spikes?	2	–2	
b. Laboratory duplicates?	2	–2	
c. Surrogate recoveries?	2	–2	
d. Calibration check standards?	2	–2	
15. Have method detection limit studies been performed for each method in use?	5	–2	
a. How recently? _____			
b. Any procedural or configurational changes since then?	–2	2	
16. Do records indicate that appropriate corrective action has been taken when analytical results fail to meet the QC criteria?	5	–2	

Comments: _____

G. QC Manual Checklist

1. Does the laboratory have a QC manual?	10	–10	
2. Does the manual address the following:			
a. Personnel?	1	–1	
b. Facilities or equipment?	1	–1	
c. Operation of instruments?	1	–1	
d. Method validation	1	–1	
e. Calibration frequency	1	–2	
f. Standards preparation	1	–1	
g. Documentation of procedures	1	–1	
h. Preventive maintenance	1	–1	
i. Reliability of data	1	–2	
j. Data validation	1	–2	
k. Feedback and corrective action	1	–2	
l. Record-keeping	1	–2	
m. Internal audits	1	–1	

Comments: _____

		Yes	No	Comments
H.	**Summary**			
1.	Do responses to the evaluation indicate that laboratory personnel are aware of QA/QC and its potential impact on the data?	2	–2	
2.	Is a positive emphasis placed on QA/QC by laboratory management?	2	–2	
3.	Have the responses been open and direct?	2	–2	
4.	Has the attitude been cooperative?	2	–2	
5.	Is the proper emphasis placed on quality assurance?	2	–5	

Comments: _____

Attachment 3

This is an example memorandum for a specific laboratory for which there were very few negative remarks. Naturally, not all laboratories will be of this quality.

EXAMPLE MEMORANDUM

(from an actual laboratory audit)

TO: [Audit Requestor]

FROM: [Auditor]

DATE: [Day/Month/Year]

SUBJECT: Laboratory Audit Visit to [Laboratory Name]
[Street Address]
[City, State, Zip Code]
[Phone Number]

An analytical chemistry laboratory observation visit was conducted on [date] at the [laboratory name and location]. The observation visit was performed by [auditor name] as part of the general QA/QC observations being conducted on behalf of [client name]. Samples were collected in the field by [source testing or field sampling company], and analyzed at the [laboratory name]. The following areas were included as a part of the observation process at [laboratory name]:

- Personnel and organization
- Sample receipt and storage
- Sample preparation facilities
- Instrumentation and equipment
- Quality control
- Data handling and review.

The attached Analytical Chemistry Laboratory Audit Guidelines were followed during the visit. Participating [laboratory name] staff included:

- [Names and titles].

The purpose of the observation visit was to determine whether [laboratory name] has the facilities, equipment, trained personnel, and QA/QC program in place to be capable of routinely producing data of known quality for site characterization programs. The completed checklist is appended.

AUDIT FINDINGS

Generally, the [laboratory name] was found to be capable of producing known quality, traceable data. There appeared to be an adequate understanding of QA/QC procedures within the laboratory. The employees interviewed displayed a positive attitude and an appreciation for the importance of quality assurance, and understood the potential impact of QA/QC upon data.

No major deficiencies were noted during the audit. The following recommendations are intended to improve a basically sound program:

- There should be more formal in-house QA/QC and training programs instituted for analysts and technicians; currently, training is dependent upon the more experienced analysts

- An inspection checklist should be generated for incoming samples, which includes the nature and condition of samples and documentation
- Internal chain-of-custody procedures should be initiated
- As part of the SOPs, a specific policy should be instituted for the rejection of incoming compromised samples
- Control charts should be maintained for all types of QC samples that are run.

The [laboratory name] staff were very helpful and cooperative. There appears to be a positive emphasis placed on QA/QC by laboratory management, and the responses appeared to be open and direct.

APPENDIX H

Format for the Sediment Testing Report

SEDIMENT TESTING REPORT FORMAT

The sediment testing report, including physical, chemical, bioassay, and bioaccumulation data, should be prepared using the format guidelines below.

A. INTRODUCTION

The project description should include the following information:

1. Location of the proposed dredging project and the disposal site.

2. A plan view map showing project design depth, side-slopes, allowable overdepth.

3. Proposed dredging and disposal quantities.

B. MATERIALS AND METHODS

1. Field sediment sampling and sediment sample handling procedures should be described or referenced.

2. References for laboratory protocols for physical, chemistry, bioassay, and bioaccumulation analyses should be included, such as:

   a. EPA method numbers and other EPA-approved methods that do not have a specific EPA number.

   b. Target detection limits and references used for physical, chemical and tissue analyses.

   c. Test species used in each test, the supplier or collection site for each test species, and QA/QC procedures for maintaining the test species.

   d. Locations of references and control sediment samples.

   e. Source of water used in all biological tests and documentation that the water is free of contaminants.

   f. Bioassay and bioaccumulation testing procedures and QA/QC information.

   g. Statistical analysis procedures.

C. LOCATION OF SAMPLING AREAS

1. The exact position of the dredging site sampling areas and each core taken within each sampling area should be mapped.

2. A table should be prepared with the coordinates for each station in latitude and longitude (North America Datum 1983).

3. A table should be included showing the required sampling depth at each sampling location compared to the actual core depth achieved during field sampling. Any problems in collecting sediment from the required depth should be discussed.

4. The type of positioning equipment to be used for the sampling program should be specified.

5. Charts should be provided to show the location of the reference site, the control site(s) and the disposal site, including the coordinates of each site.

D. DESCRIPTION OF TESTING APPROACH

The rationale for performing specific types of tests (e.g. chemical analysis of elutiate for comparison to water quality standards, tissue analysis, etc.) should be presented in writing.

E. FINAL RESULTS

1. Summary data tables should be furnished. All data tables should be typed or produced as a computer printout.

2. Copies of the final raw data sheets should be included. These tables should be certified to be accurate by the analytical laboratory manager.

F. DISCUSSION AND ANALYSIS OF DATA

1. An evaluation of historical data from the proposed dredging site should be concisely discussed. References to previous sediment testing should also be included.

2. Statistical comparisons between the dredging site sediments and the reference sediment should be made.

G. REFERENCES

This list should include all references used in the field sampling program, laboratory and statistical data analyses, and historical data used to compare the dredging to the reference site.

H. DETAILED QA/QC PLANS AND INFORMATION

The following topics should be addressed in the QA Plan:

- Introductory material, including title and signature pages, table of contents, and project description.

- QA organization and responsibilities (the QA organization should be designed to operate with a degree of independence from the technical project organization to ensure appropriate oversight)
- QA objectives
- Standard Operating Procedures
- Sampling strategy and procedures
- Sample custody
- Calibration procedures and frequency
- Analytical procedures
- Data validation, reduction, and reporting
- Internal QC checks
- Performance and system audits
- Facilities
- Preventive maintenance
- Calculation of data quality indicators
- Corrective actions
- QA reports to management
- References.

I. PERTINENT CORRESPONDENCE WITH SCOPING COMMENTS AND COORDINATION

The report should contain copies of the correspondence related to coordination on the testing activities for the proposed project.

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