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Superfund

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK FOR INORGANICS ANALYSIS

MULTI-MEDIA, MULTI-CONCENTRATION

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USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR

INORGANICS ANALYSIS

Multi-Media

Multi-Concentration

Document Number ILM02.0

Including Revision ILM02.1 (September 1991)

ATTACHMENT A

STATEMENT OF WORK

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EXHIBIT A

SUMMARY OF REQUIREMENTS

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SECTION I
GENERAL REQUIREMENTS

The Contractor shall employ procedures specified in this Statement of Work (SOW) in the preparation and analysis of aqueous (water) and solid (soil/sediment) samples for the presence and quantitation of 23 indicated elements and cyanide.

The Contractor shall use proven instruments and techniques to identify and measure the elements and inorganic species presented in the Target Analyte List (Exhibit C). The Contractor shall perform sample preparation and analysis procedures as prescribed in Exhibit D, meeting specified sample preservation and holding time requirements.

If dissolved metals are requested by the EPA Regional offices, the Contractor shall follow the instructions provided on the Traffic Reports. If there are no instructions on the Traffic Report, the Contractor shall contact SMO for resolution.

The Contractor shall adhere to the quality assurance/quality control protocol specified in Exhibit E for all samples analyzed under this contract.

Following sample analysis, the Contractor shall perform data reduction and shall report analytical activities, sample data, and quality control documentation as designated in Exhibit B.

Exhibit F contains chain-of-custody and document control requirements which the Contractor must follow in processing samples and specifies requirements for written laboratory standard operating procedures.

To ensure proper understanding of language utilized in this contract, Exhibit G contains a glossary of terms. When a term is used in the text without explanation, the glossary meaning shall be applicable. Glossary definitions do not replace or take precedence over specific information included in the SOW text.

Exhibit H contains the Agency Standard implementation for reporting data electronically.

The samples to be analyzed by the Contractor are from known or suspected hazardous waste sites and, potentially, may contain hazardous inorganic and/or organic materials at high concentration levels. The Contractor should be aware of the potential hazards associated with the handling and analyses of these samples. It is the Contractor's responsibility to take all necessary measures to ensure the health and safety of its employees.

In addition, the Contractor must be aware of the importance of maintaining the integrity of the data generated under the contracts as it is used to make major decisions regarding public health and environmental welfare. The data may also be used in litigation against Potentially Responsible Parties in the enforcement of Superfund legislation.

Prior to accepting any samples from the Agency, the Contractor shall have, in house, the appropriate standards for all target analytes listed in Exhibit C.

SECTION II
SPECIFIC REQUIREMENTS

A. FOR EACH SAMPLE, THE CONTRACTOR SHALL PERFORM THE FOLLOWING TASKS:

Task I: Receive and Prepare Hazardous Waste Samples.

1. The Contractor shall receive and handle samples under the chain-of-custody and sample documentation procedures described in Exhibit F. A sample consists of all components, perhaps more than one phase, contained inside appropriate receptacles. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.

2. The Contractor shall provide the required analytical expertise and instrumentation for analyses of Target Analyte List (TAL) elements and cyanide equal to or lower than the detection limits specified in Exhibit C. In Exhibit D, EPA provides the Contractor with the specific sample preparation techniques for water and soil/sediment samples and the analytical procedures which must be used. A schematic flow chart depicting the complete low level-medium level inorganics analytical scheme is presented in Section I of Exhibit D.

3. The Contractor shall prepare and analyze samples within the maximum holding time specified in Section II of Exhibit D even if these times are less than the maximum data submission time allowed in this contract.

4. The Contractor is advised that the samples received under this contract are usually from known or suspected hazardous waste sites and may contain high (greater than 15%) levels of organic and inorganic materials of a potentially hazardous nature and of unknown structure and concentration, and should be handled throughout the analysis with appropriate caution. It is the Contractor's responsibility to take all necessary measures to ensure laboratory safety.

Task II: Analyze Samples for Identity and Quantitation of Specific Inorganic Constituents.

1. For each sample received, the Contractor may be required to perform the analyses described in the following paragraphs 2., 3. and 4. The documentation that accompanies the sample(s) to the Contractor facility shall indicate specific analytical requirements for that sample or set of samples.

2. Exhibit D specifies the analytical procedures that must be used. Exhibit D contains instructions and references for preparation of samples containing low-to-medium concentrations of inorganics for ICP analysis; flame, graphite furnace and cold vapor AA analysis and cyanide analysis. The identification and quantitation of

analytes other than cyanide shall be accomplished using the ICP or AA methods specified in Exhibit D and achieves the Contract Required Detection Limit (CRDL) specified in Exhibit C. Cyanide shall be analyzed by the individual procedures specified in Exhibit D.

3. All samples must initially be run undiluted (i.e., the final product of sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range, appropriate dilution (but not below the CRDL) and reanalysis of the prepared sample is required, as specified in Exhibit D.

4. For the purpose of this contract, a full sample analysis is defined as the analysis for ALL of the target constituents identified in Exhibit C in accordance with the methods in Exhibit D and performance of related QA/QC as specified in Exhibit E. Duplicate sample, laboratory control sample, and spike sample analyses shall each be considered a separate full sample analysis. All other QA/QC requirements are considered an inherent part of this contract Statement of Work and are included in the contract sample unit price.

Task III: Perform Required Quality Assurance/Quality Control Procedures

1. All specific QA/QC procedures prescribed in Exhibit E shall be strictly adhered to by the Contractor. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and shall be reported in accordance with Exhibit B requirements.

2. The Contractor shall establish and use on a continuing basis QA/QC procedures including the daily or (as required) more frequent use of standard reference solutions from EPA, the National Institute of Standards and Technology or secondary standards traceable thereto, where available at appropriate concentrations (i.e., standard solutions designed to ensure that operating parameters of equipment and procedures, from sample receipt through identification and quantitation, produce reliable data). Exhibit E specifies the QA/QC procedures required.

3. The Contractor shall establish a Quality Assurance Plan (QAP) as defined in Exhibit E with the objective of providing sound analytical chemical measurements. This program shall incorporate the quality control procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

4. Additional quality assurance and quality control shall be required in the form of Performance Evaluation Samples submitted by EPA for Contractor analysis, and in the form of verification of instrument parameters, as described in Exhibit E.

5. Laboratory Control Sample (LCS) - This standard solution is designed to assure that the operating parameters of the analytical instrumentation and analytical procedures from sample preparation through identification and quantitation produce reliable data. The Contractor must analyze the LCS concurrently with the analysis of the samples in the Sample Delivery Group (see Exhibit A, Part I).

B. EPA has provided to the Contractor formats for the reporting of data (Exhibits B and H). The Contractor shall be responsible for completing and returning analysis data sheets and submitting computer-readable data on diskette in the format specified in this SOW and within the time specified in the Contract Performance/Delivery Schedule (see Exhibit B).

1. Use of formats other than that designated by EPA will be deemed as noncompliant. Such data are unacceptable. Resubmission in the specified format at no additional cost to the government will be required.

2. Computer generated forms may be submitted in the hardcopy data package(s) provided that the forms are in EXACT EPA FORMAT. This means that the order of data elements is the same as on each EPA required form, including form numbers and titles, page numbers and header information, columns and lines.

3. The data reported by the Contractor on the hardcopy data forms and the associated computer-readable data submitted by the Contractor on diskette must contain identical information. If during government inspection discrepancies are found, the Contractor shall be required to resubmit either or both sets of data at no additional cost to the Government. The resubmitted diskette and/or hardcopy must contain all of the initially correct information previously submitted for all samples including the Laboratory Control Sample, standards, and blanks in the SDG in addition to the corrections replacing the variables which were incomplete or incorrect according to the requirements in the SOW.

C. The Contractor shall provide analytical equipment and technical expertise for this contract as specified by the following:

1. Inductively coupled plasma (ICP) emission spectrometer with the capability to analyze metals sequentially or simultaneously.

2. Atomic absorption (AA) spectrometer equipped with graphite furnace, flame, and cold vapor AA (or a specific mercury analyzer) analysis capabilities.

3. Analytical equipment/apparatus for analysis of cyanide as described in Exhibit D.

D. The minimum functional requirements necessary to meet the terms and conditions of this contract are listed in items 1-7 below. The Contractor shall designate and utilize qualified key personnel to

perform these functions. The EPA reserves the right to review personnel qualifications and experience. See Section III, Technical & Management Requirements.

1. Inorganic Laboratory Supervisor
2. Quality Assurance Officer
3. Systems Manager
4. Programmer Analyst
5. ICP Spectroscopist
6. ICP Operator
7. Atomic Absorption (AA) Operator
8. Inorganic Sample Preparation Specialist
9. Classical Techniques (Cyanide) Analyst
10. Inorganic Chemist (Backup)

E. The Contractor shall respond (within seven days) to written requests from data recipients for additional information or explanations that result from the Government's inspection activities unless otherwise specified in the contract (see Exhibit E for details on Government inspection activities).

F. The Contractor is required to retain unused sample volume and used sample containers for a period of 60 days after data submission. From time of receipt until analysis, the Contractor shall maintain soil/sediment samples at $4^{\circ}C$ ($\pm 2^{\circ}C$).

G. The Contractor shall adhere to chain-of-custody and document control procedures described in Exhibit F. Documentation, as described therein, shall be required to show that all procedures are being strictly followed. This documentation shall be reported in the Complete SDG File (see Exhibit B).

H. Sample shipments to the Contractor's facility will be scheduled and coordinated by the EPA CLP Sample Management Office (SMO), acting on behalf of the Administrative Project Officer. The Contractor shall communicate with SMO personnel by telephone as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed.

If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation/paperwork (e.g., Traffic Reports not with shipment, or sample and Traffic Report numbers do not correspond) the Contractor shall immediately contact SMO for resolution. The Contractor shall immediately notify SMO regarding any problems and/or laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall immediately notify SMO personnel in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

I. Sample analyses will be scheduled by groups of samples, each defined as a Case and identified by a unique EPA Case number assigned by SMO. A Case signifies a group of samples collected at one site or geographical

area over a finite time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case. A Case consists of one or more Sample Delivery Groups (SDG). An SDG is defined by the following, whichever is most frequent:

- each Case of field samples received, OR
- each 20 field samples within a Case, OR
- each 14 calendar day period during which field samples in a Case are received (seven calendar day period for 14-day data turnaround contracts), said period begins with the receipt of the first sample in the SDG.

Samples may be assigned to Sample Delivery Groups by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory. Such assignment must be made at the time the samples are received, and may not be made retroactively.

Data for all samples in an SDG must be submitted together (in one package) in the order specified in Exhibit B. The SDG number is the EPA sample number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number is the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. The SDG number is reported on all data reporting forms. The SDG Receipt Date is the day that the last sample in the SDG is received.

The Contractor is responsible for identifying each SDG as samples are received, through proper sample documentation (see Exhibit B) and communication with SMO personnel.

J. Each sample received by the Contractor will be labeled with an EPA sample number, and accompanied by a Traffic Report form bearing the sample number and descriptive information regarding the sample. EPA field sample numbers are six digits in length. If the Contractor receives a sample number of any other length, contact SMO immediately. The Contractor shall complete and sign the Traffic Report, recording the date of sample receipt and sample condition on receipt for each sample container. The Contractor must also follow the instructions given on the Traffic Report in choosing the QC samples when such information is provided.

The Contractor shall submit signed copies of Traffic Reports for all samples in a Sample Delivery Group to SMO within three calendar days following receipt of the last sample in the SDG. Traffic Reports shall be submitted in SDG sets (i.e., all Traffic Reports for an SDG shall be clipped together) with an SDG Cover Sheet containing information regarding the Sample Delivery Group, as specified in Exhibit B.

K. EPA Case numbers (including SDG numbers) and EPA sample numbers shall be used by the Contractor in identifying samples received under this contract both verbally and in reports/correspondence.

L. Samples will routinely be shipped directly to the Contractor through a delivery service. The Contractor shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays and holidays. As necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Contractor's geographical area.

M. The Contractor shall accept all samples scheduled by SMO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

SECTION III
TECHNICAL AND MANAGMENT REQUIREMENTS

I. TECHNICAL CAPABILITY

As cited in Section II the Contractor shall have the following technical and management capabilities. Note: For those technical functions which require a minimum educational degree and experience, an advanced degree in chemistry or any scientific/engineering discipline, (e.g., Master's or Doctorate) does not substitute for the minimum experience requirements.

Any personnel changes affecting the key personnel as stated in Exhibit A, Section III, Items I and II, shall require the Contractor to notify in writing the Technical Project Officer and the Administrative Project Officer within 14 days of the personnel change. The Contractor shall provide a detailed resume to the Technical Project Officer, Administrative Project Officer, and EMSL/LV for the replacement personnel within 14 days of the Contractor's assignment of the personnel. The resume shall include position description of titles, education (pertinent to this contract), number of years of experience (pertinent to this contract) month and year hired, previous experience and publications.

A. Technical Supervisory Personnel/Key Personnel

1. Inorganics Laboratory Supervisor

a. Responsible for all technical efforts of the Inorganics Laboratory to meet all terms and conditions of the EPA contract.

b. Qualifications

(1) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience:

Minimum of three years of laboratory experience, including at least one year in a supervisory position.

2. Quality Assurance Officer

a. Responsible for overseeing the quality assurance aspects of the data and reporting directly to upper management to meet all terms and conditions of the EPA contract.

b. Qualifications:

(1) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience:

Minimum of three years of laboratory experience, including at least one year of applied experience with QA principles and practices in an analytical laboratory.

3. Systems Manager

a. Responsible for the management and quality control of all computing systems (hardware. software, documentation and procedures), generating, updating, and performing quality control reviews of automated deliverables to meet all terms and conditions of the EPA contract.

b. Qualifications:

(1) Education:

Minimum of Bachelor's degree with four or more intermediate courses in programming, information management, database management systems, or systems requirements analysis.

(2) Experience:

Minimum of three years experience in data or systems management or programming including one year experience with the software being utilized for data management and generation of deliverables.

4. Programmer Analyst

a. Responsible for the installation, operation and maintenance of software and programs, generating, updating and performing quality control reviews of analytical databases and automated deliverables to meet all terms and conditions of the EPA contract.

b. Qualifications:

(1) Education:

Minimum of Bachelor's degree with four or more intermediate courses in programming, information management, information systems, or systems requirements analysis.

(2) Experience:

Minimum of two years experience in systems or applications programming including one year of experience with the software being utilized for data management and generation of deliverables.

B. Technical Staff

1. ICP Spectroscopist Qualifications

a. Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

Specialized training in ICP Spectroscopy.

b. Experience:

Minimum of two years of applied experience with ICP analysis of environmental samples.

2. ICP Operator Qualifications

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline with one year of experience in operating and maintaining ICP instrumentation, or, in lieu of the educational requirement, three additional years of experience in operating and maintaining ICP instrumentation.

3. Atomic Absorption (AA) Operator Qualifications

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline with one year of experience in operating and maintaining AA instrumentation for graphite furnace, flame, and cold vapor AA, or, in lieu of the educational requirement, three additional years of experience in operating and maintaining AA instrumentation, including graphite furnace, flame, and cold vapor techniques.

4. Inorganic Sample Preparation Specialist Qualifications

a. Education:

Minimum of high school diploma and a college level course in general chemistry or equivalent.

b. Experience:

Minimum of 1 year of experience in sample preparation in an analytical laboratory.

c. Experience (Required if microwave digestion is used):

Minimum of six months experience in an analytical laboratory and six months experience in sample dissolution using microwave digestion techniques.

5. Classical Techniques (Cyanide) Analyst Qualifications

a. Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

b. Experience:

Minimum of 1 year of experience with classical chemistry laboratory procedures, in conjunction with the educational qualifications; or, in lieu of educational requirement, two years of additional equivalent experience.

6. Technical Staff Redundancy

In order to ensure continuous operations to accomplish the required work as specified by the EPA contract, the bidder shall have a minimum of one (1) chemist available at all times as a back-up technical person with the following qualifications.

a. Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

b. Experience:

Minimum of one year of experience in each of the following areas -

- o ICP operation and maintenance
- o AA operation and maintenance
- o Classical chemistry analytical procedures
- o Sample preparation for inorganics analysis

C. Facilities

The adequacy of the facilities and equipment is of equal importance for the technical staff to accomplish the required work as specified by the EPA contract.

1. Sample Receipt Area

   Adequate, contamination-free, well-ventilated work space provided with chemical resistant bench top for receipt and safe handling of EPA samples.

2. Storage Area

   Sufficient refrigerator space to maintain unused EPA sample volume for 60 days after data submission. Soil samples must be stored in a refrigerator at 4°C (±2°C). Samples and standards must be stored separately to prevent cross-contamination.

3. Sample Preparation Area

   Adequate, contamination-free, well-ventilated work space provided with:

   a. Benches with chemical resistant tops.

   b. Exhaust hoods. Note: Standards must be prepared in a glove box or isolated area.

   c. Source of distilled or demineralized organic-free water.

   d. Analytical balance(s) located away from draft and rapid change in temperature.

D. Instrumentation

At a minimum, the Contractor shall have the following instruments operative at the time of the Preaward Site Evaluation and committed for the full duration of the contract.

1. Primary Instrument Requirements for 200 Samples/Month Capacity Requirements

Fraction	No. of Instrument(s)	Type of Instrument
ICP Metals	1	ICP Emission Spectrophotometer
GFAA Metals	2	Atomic Absorption Spectrophotometer with Graphite Furnace Atomizer
Mercury	2	Mercury Cold Vapor AA Analyzer or AA instrument modified for Cold Vapor Analysis
Cyanide	12 distillation units + 1 photometer	See Cyanide Methods, Statement of Work Exhibit D, Section IV, Part E

There are no Secondary Instrument Requirements for 200 Samples/Month Capacity.

2. 300 Samples/Month Capacity Requirements

Fraction	No. of Instrument(s)	Type of Instrument
ICP Metals	1	ICP Emission Spectrophotometer
GFAA Metals	3	Atomic Absorption Spectrophotometer with Graphite Furnace Atomizer
Mercury	2	Mercury Cold Vapor AA Analyzer or AA instrument modified for Cold Vapor Analysis
Cyanide	18 distillation units + 1 photometer	See Cyanide Methods, Statement of Work Exhibit D, Section IV, Part E

Secondary Instrument Requirements for 300 Samples/Month Capacity

The Contractor shall have the following instruments in place and operational at any time as a back-up system:

Quantity	Instruments
One	GFAA

3. Additional Instrument Requirements for greater than 300 Samples/Month Capacity

Quantity	Instruments
One	GFAA
One	ICP Emission Spectrophotometer

4. Instrument Specifications

Further information on instrument specifications and required ancillary equipment may be found in the Statement of Work.

E. Data Management and Handling

1. Hardware - Contractor will have an IBM or IBM-compatible mini-computer or PC capable of recording required sample data on 5.25 inch double-sided, double-density 360 K-byte or high density 1.2 M-byte diskettes; or a 3.5 inch double-sided, double-density 720 K-byte or 1.44 M-byte diskettes in ASCII text file format and in accordance with the file, record and field specifications listed in the SOW, Exhibit H.

   Other minimum requirements include:

   Hard disk of at least 20 M-bytes.

   Asynchronous, Hayes-compatible modem capable of at least 2,400 baud transmission speed. In addition, MNP level 5 compatibility or compatibility with EPA V.32/V.42bis equipment is recommended.

2. Software - Software, utilized in generating, updating and providing quality control for analytical databases and automated deliverables shall have the following additional capabilities:

   Editing and updating databases.

   Controlled access using user ID and file password protection.

3. The Contractor shall also be able to submit reports and data packages as specified in the SOW Exhibit B. To complete this task, the Contractor shall be required to provide space, tables and adequate copy machines to meet the contract requirements.

II. LABORATORY MANAGEMENT CAPABILITY

The Contractor must have an organization with well-defined responsibilities for each individual in the management system to ensure sufficient resources for EPA contract(s) and to maintain a successful operation. To establish this capability, the Contractor shall designate personnel to carry out the following responsibilities for the EPA contract. Functions include, but are not limited to, the following:

A. Technical Staff

Responsible for all technical efforts for the EPA contract.

B. Project Manager

Responsible for overall aspects of EPA contract(s) (from sample receipt through data delivery), and shall serve as the primary contact for EPA Headquarters Administrative Project Officer and Regional Technical Project Officers.

C. Sample Custodian

Responsible for receiving the EPA samples (logging, handling and storage).

D. Quality Assurance Officer

Responsible for overseeing the quality assurance aspects of the data and reporting directly to upper management.

E. Document Control Officer

Responsible for all aspects of data deliverables: organization, packaging, copying, and delivery. Responsible for ensuring that all documents generated are placed in the complete SDG file for inventory and are delivered to the appropriate EPA Regional personnel or other receiver.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

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SECTION I

CONTRACT REPORTS/DELIVERABLES DISTRIBUTION
(For 35-Day Turnaround Contracts)

The following table reiterates the Contract reporting and deliverables requirements specified in the Contract Schedule and specifies the distribution that is required for each deliverable. NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Administrative Project Officer will notify the Contractor in writing of such changes when they occur.

Item	No. Copies	Delivery Schedule	Distribution (1)	(2)	(3)	(4)
*****A. Standard Operating Procedures	3	60 days after contract award and as required in Exhibit E.		X	X	X
B. Sample Traffic Reports	1	3 days after receipt of last sample in Sample Delivery Group (SDG)***	X			
***C. Sample Data Package	2	35 days after receipt of last sample in SDG	X		X	
D. Data in Computer Readable Format	1	35 days after receipt of last sample in SDG	X			
****E. Complete SDG File	1	35 days after receipt of last sample in SDG**		X		
*F. Quarterly/Annual Verification of Instrument Parameters	2	Quarterly: 15th day of January, April July, October	X		X	
*****G. Quality Assurance Plan	3	60 days after contract award and as required in Exhibit E.	As directed			

Distribution:
(1) Sample Management Office (SMO)
(2) Region-Client
(3) Environmental Monitoring Systems Laboratory (EMSL/LV)
(4) NEIC

SECTION I

CONTRACT REPORTS/DELIVERABLES DISTRIBUTION
(For 14-Day Turnaround Contracts)

The following table reiterates the Contract reporting and deliverables requirements specified in the Contract Schedule and specifies the distribution that is required for each deliverable. NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Administrative Project Officer will notify the Contractor in writing of such changes when they occur.

Item	No. Copies	Delivery Schedule	Distribution (1)	(2)	(3)	(4)
*****A. Standard Operating Procedures	3	60 days after contract award and as required in Exhibit E.		X	X	X
B. Sample Traffic Reports	1	3 days after receipt of last sample in Sample Delivery Group (SDG)***	X			
***C. Sample Data Package	2	14 days after receipt of last sample in SDG	X		X	
D. Data in Computer Readable Format	1	14 days after receipt of last sample in SDG	X			
****E. Complete SDG File	1	14 days after receipt of last sample in SDG**		X		
*F. Quarterly/Annual Verification of Instrument Parameters	2	Quarterly: 15th day of January, April July, October	X		X	
*****G. Quality Assurance Plan	3	60 days after contract award and as required in Exhibit E.	As directed			

Distribution:
(1) Sample Management Office (SMO)
(2) Region-Client
(3) Environmental Monitoring Systems Laboratory (EMSL/LV)
(4) NEIC

* Also required in each Sample Data Package.

** Concurrent delivery of these items to all recipients is required.

*** Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 14 days or less (seven days or less for 14-day data turnaround contracts) and not exceeding 20 samples. Data for all samples in the SDG are due concurrently. (See SOW Exhibit A, for further description).

**** Complete SDG file will contain the original sample data package plus all of the original documents described in Exhibit B of the Statement of Work under Complete SDG File.

*****See Exhibit E for description

NOTE: As specified in the Contract Schedule (Government Furnished Supplies and Materials), unless otherwise instructed by the CLP Sample Management Office, the Contractor shall dispose of unused sample volume and used sample bottles/containers no earlier than sixty (60) days following submission of analytical data.

Distribution Addresses:

(1) USEPA Contract Laboratory Program (CLP)
Sample Management Office (SMO)
P. O. Box 818
Alexandria, VA 22313

For overnight delivery service, use street address:
300 N. Lee Street
Alexandria, VA 22313

(2) USEPA REGIONS: The CLP Sample Management Office, acting on behalf of the Administrative Project Officer, will provide the Contractor with the list of addressees for the ten EPA Regions. SMO will provide the Contractor with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

(3) USEPA Environmental Monitoring Systems Laboratory (EMSL/LV)
944 E. Harmon Avenue
Las Vegas, NV 89109
Attn: Data Audit Staff

(4) USEPA National Enforcement Investigations Center (NEIC)
Attn: CLP Audit Program
Denver Federal Center Bldg. 53
P.O. Box 25227
Denver, CO 80225

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

The Contractor laboratory shall provide reports and other deliverables as specified in the Contract Performance/Delivery Schedule (see Contract Schedule, Section F). The required content and form of each deliverable is described in this Exhibit.

All reports and documentation MUST BE as follows:

- Legible,
- Clearly labeled and completed in accordance with instructions in this Exhibit,
- Arranged in increasing alphanumeric EPA sample number order
- Paginated sequentially according to instructions in this Exhibit, and
- Single-sided.

If submitted documentation does not conform to the above criteria, the Contractor will be required to resubmit such documentation with deficiency(ies) corrected, at no additional cost to the government.

The Contractor must be prepared to receive the full monthly sample contract requirement at the time of contract award.

Whenever the Contractor is required to submit or resubmit data as a result of an on-site laboratory evaluation or through an Administrative Project Officer (APO)/Technical Project Officer (TPO) action, or through a Regional data reviewer's request, the data must be clearly marked as ADDITIONAL DATA and must be sent to all three contractual data recipients (SMO, EMSL/LV, and Region). A cover letter shall be included which describes what data is being delivered, to which EPA Case(s) the data pertains, and <u>who requested the data</u>.

Whenever the Contractor is required to submit or resubmit data as a result of Contract Compliance Screening (CCS) review by SMO, the data must be sent to all three contractual data recipients (SMO, EMSL/LV and Region), and in all three instances must be accompanied by a color-coded COVER SHEET (Laboratory Response To Results of Contract Compliance Screening) provided by SMO. Diskette deliverables need only be submitted or resubmitted to SMO. Revised DC-1 and DC-2 forms shall be resubmitted to SMO.

Section IV of this Exhibit contains the required Inorganic Analysis Data Reporting Forms in Agency-specified formats; Section III of this Exhibit contains instructions to the Contractor for properly completing all data reporting forms to provide the Agency with all required data. Data elements and field descriptors for reporting data in computer-readable format are contained in Exhibit H.

Descriptions of the requirements for each deliverable item cited in the Contract Performance/Delivery Schedule (see Contract Schedule, Section F) are specified in parts A-G of this Section. Items submitted concurrently must be arranged in the order listed. Additionally, the components of each item must be arranged in the order presented herein when the item is submitted.

A. Quality Assurance Plan and Standard Operating Procedures

See Exhibits E and F for requirements.

B. Sample Traffic Reports

Original Sample Traffic Report page marked "Lab Copy for Return to SMO" with lab receipt information and signed with original Contractor signature, shall be submitted for each sample in the Sample Delivery Group.

Traffic Reports (TRs) shall be submitted in Sample Delivery Group (SDG) sets (i.e., TRs for all samples in an SDG shall be clipped together), with an SDG Cover Sheet attached.

The SDG Cover Sheet shall contain the following items:

- Lab name
- Contract number
- Sample Analysis Price - full sample price from contract.
- Case Number
- List of EPA sample numbers of all samples in the SDG, identifying the first and last samples received, and their dates of receipt.

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the sample with the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the sample with the highest sample number (considering both alpha and numeric designations).

In addition, each Traffic Report must be clearly marked with the SDG Number, the sample number of the first sample in the SDG (as described in the following paragraph). This information should be entered below the Lab Receipt Date on the TR.

EPA field sample numbers are six digits in length. If the Contractor receives sample numbers of any other length, contact SMO immediately. The EPA sample number of the first sample received in the SDG is the SDG number. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. (The SDG number is also reported on all data reporting forms. See Section III, Form Instruction Guide.)

If samples are received at the laboratory with multi-sample Traffic Reports (TRs), all the samples on one multi-sample TR may not necessarily be in the same SDG. In this instance, the laboratory must make the appropriate number of photocopies of the TR, and submit one copy with each SDG cover sheet.

C. Sample Data Package

The sample data package shall include data for analysis of all samples in one Sample Delivery Group (SDG), including field and analytical samples, reanalyses, blanks, spikes, duplicates, and laboratory control samples.

The sample data package must be complete before submission, must be consecutively paginated (starting with page number one and ending with the number of all pages in the package), and shall include the following:

1. Cover Page for the Inorganic Analyses Data Package, (COVER PAGE -- Inorganic Analyses Data Package), including: laboratory name; laboratory code; contract number; Case No.; Sample Delivery Group (SDG) No.; SAS Number (if appropriate); EPA sample numbers in alphanumeric order showing EPA sample numbers cross-referenced with lab ID numbers; comments, describing in detail any problems encountered in processing the samples in the data package; and, completion of the statement on use of ICP background and interelement corrections for the samples.

   The Cover Page shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on diskette has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature." This statement shall be directly followed by the signature of the Laboratory Manager or his designee with a typed line below it containing the signers name and title, and the date of signature.

   In addition, on a separate piece of paper, the Contractor must also include any problems encountered; both technical and administrative, the corrective action taken, and the resolution.

   The Contractor shall retain a copy of the Sample Data Package for 365 days after final acceptance of data. After this time, the Contractor may dispose of the package.

2. Sample Data

   Sample data shall be submitted with the Inorganic Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric EPA sample number order, followed by the QC analyses data, Quarterly Verification of Instrument Parameters forms, raw data, and copies of the digestion and distillation logs.

   a. Results -- Inorganic Analysis Data Sheet [FORM I - IN]

      Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot verify all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

      Appropriate concentration units must be specified and entered on Form I. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid samples must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is

greater than or equal to 10. Results for percent solids must be reported to one decimal place. The preceding discussion concerning significant numbers applies to Forms I and X only. For other Forms, follow the instructions specific to those forms as contained in this exhibit.

b. Quality Control Data

1) Initial and Continuing Calibration Verification [FORM II (PART 1) - IN]

2) CRDL Standard for AA and ICP [FORM II (PART 2) - IN]

3) Blanks [FORM III - IN]

4) ICP Interference Check Sample [FORM IV - IN]

5) Spike Sample Recovery [FORM V (PART 1) - IN]

6) Post Digest Spike Sample Recovery [FORM V (PART 2) - IN]

7) Duplicates [FORM VI - IN]

8) Laboratory Control Sample [FORM VII - IN]

9) Standard Addition Results [FORM VIII - IN]

10) ICP Serial Dilutions [FORM IX - IN]

11) Preparation Log [Form XIII - IN]

12) Analysis Run Log [Form XIV - IN]

c. Quarterly Verification of Instrument Parameters

1) Instrument Detection Limits (Quarterly) [FORM X - IN]

2) ICP Interelement Correction Factors (Annually) [FORM XI (PART 1) - IN]

3) ICP Interelement Correction Factors (Annually) [FORM XI (PART 2) - IN]

4) ICP Linear Ranges (Quarterly) [FORM XII - IN]

(Note that copies of Quarterly Verification of Instrument Parameters forms for the current quarter must be submitted with each data package.)

d. Raw Data

For each reported value, the Contractor shall include in the data package all raw data used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as all sample analysis results. This statement does not apply to the Quarterly Verification of Instrument Parameters submitted as a part

of each data package. Raw data must contain all instrument readouts used for the sample results. Each exposure or instrumental reading must be provided, including those readouts that may fall below the IDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the instruments direct sequential readout must be included. A hardcopy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be: ICP, Flame AA, Furnace AA, Mercury, and Cyanide. All raw data shall include concentration units for ICP and absorbances or concentration units for flame AA, furnace AA, Mercury and Cyanide. All flame and furnace AA data shall be grouped by element.

Raw data must be labeled with EPA sample number and appropriate codes, shown in Table 1 following, to unequivocally identify:

1) Calibration standards, including source and prep date.

2) Initial and continuing calibration blanks and preparation blanks.

3) Initial and continuing calibration verification standards, interference check samples, ICP serial dilution samples, CRDL Standard for ICP and AA, Laboratory Control Sample and post digestion spike.

4) Diluted and undiluted samples (by EPA sample number) and all weights, dilutions and volumes used to obtain the reported values. (If the volumes, weights and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient).

5) Duplicates.

6) Spikes (indicating standard solutions used, final spike concentrations, and volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, a general statement outlining these parameters is sufficient.

7) Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation.

8) All information for furnace analysis clearly and sequentially identified on the raw data, including EPA sample number, sample and analytical spike data, percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, slope and intercepts of linear fit, final sample concentration (standard addition concentration), and type of background correction used: BS for Smith-Heiftje, BD for Deuterium Arc, or BZ for Zeeman.

9) Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide times of analysis, these must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and the CRDL standard for ICP.

10) Integration times for AA analyses.

e. Digestion and Distillation Logs

Logs shall be submitted in the following order: digestion logs for ICP, flame AA, furnace AA and mercury preparations, followed by a copy of the distillation log for cyanide. These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e., laboratory control sample, preparation blank) correspond to each batch digested, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) indication of pH <2 or >12, as applicable.

f. Properly completed Forms DC-1 and DC-2.

3. A copy of the Sample Traffic Reports submitted in Item A for all of the samples in the SDG. The Traffic Reports shall be arranged in increasing EPA Sample Number order, considering both alpha and numeric designations. A legible photocopy of the SDG cover sheet must also be submitted.

D. Data in Computer Readable Form

The Contractor shall provide a computer-readable copy of the data on reporting Forms I-XIV for all samples in the Sample Delivery Group, as specified in the Contract Performance/Delivery Schedule. Computer-readable data deliverables shall be submitted on an IBM or IBM-compatible, 5.25 inch floppy double-sided, double density 360 K-byte or a high density 1.2 M-byte diskette or on an IBM or IBM-compatible, 3.5 inch double-sided, double density 720 K-byte or a high density 1.44 M-byte diskette. The data shall be recorded in ASCII, text file format, and shall adhere to the file, record and field specifications listed in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format.

When submitted, diskettes shall be packaged and shipped in such a manner that the diskette(s) cannot be bent or folded, and will not be exposed to extreme heat or cold or any type of electromagnetic radiation. The diskette(s) must be included in the same shipment as the hardcopy data and shall, at a minimum, be enclosed in a diskette mailer.

Table 1
Codes for Labelling Data

Sample	XXXXXX
Sample not part of the SDG	ZZZZZZ
Duplicate	XXXXXXD
Matrix Spike	XXXXXXS
Serial Dilution	XXXXXXL
Analytical Spike	XXXXXXA
Post Digestion/Distillation Spike	XXXXXXA
MSA:	
Zero Addition	XXXXXX0
First Addition	XXXXXX1
Second Addition	XXXXXX2
Third Addition	XXXXXX3
Instrument Calibration Standards:	
ICP	S or S0 for blank standard
Atomic Absorption and Cyanide	S0, S10,...etc.
Initial Calibration Verification	ICV
Initial Calibration Blank	ICB
Continuing Calibration Verification	CCV
Continuing Calibration Blank	CCB
Interference Check Samples:	
Solution A	ICSA
Solution AB	ICSAB
CRDL Standard for AA	CRA
CRDL Standard for ICP	CRI
Laboratory Control Samples:	
Aqueous (Water)	LCSW
Solid (Soil/Sediment)	LCSS
Preparation Blank (Water)	PBW
Preparation Blank (Soil)	PBS
Linear Range Analysis Standard	LRS

Notes:

1. When an analytical spike or MSA is performed on samples other than field samples, the "A", "0", "1", "2" or "3" suffixes must be the last to be added to the EPA Sample Number. For instance, an analytical spike of a duplicate must be formatted "XXXXXXDA."
2. The numeric suffix that follows the "S" suffix for the standards indicates the true value of the concentration of the standard in ug/L.
3. ICP calibration standards usually consist of several analytes at different concentrations. Therefore, no numeric suffix can follow the ICP calibration standards unless all the analytes in the standard are prepared at the same concentrations. For instance, the blank for ICP must be formatted "S0."
4. Use suffixes of "0", "1", "2", "3" as appropriate for samples identified with ZZZZZZ on which MSA has been performed to indicate single injections.

E. Results of Intercomparison/Performance Evaluation (PE) Sample Analyses

Tabulation of analytical results for Intercomparison/PE Sample analyses include all requirements specified in items C. and D., above.

F. Complete SDG File (CSF)

As specified in the Delivery Schedule, one Complete SDG File (CSF) including the original Sample Data Package shall be delivered to the Region concurrently with delivery of a copy of the Sample Data Package to SMO and EMSL/LV. The contents of the CSF will be numbered according to the specifications described in Sections III and IV of Exhibit B. The Document Inventory Sheet, Form DC-2, is contained in Section IV. The CSF will contain all original documents where possible. No copies of original documents will be placed in the CSF unless the originals are bound in a logbook maintained by the laboratory. The CSF will contain all original documents specified in Sections III and IV, and Form DC-2 of Exhibit B of the SOW.

The CSF will consist of the following original documents in addition to the documents in the Sample Data Package:

1. Original Sample Data Package

2. A completed and signed Document Inventory Sheet (Form DC-2)

3. All original shipping documents, including, but not limited to, the following documents:

   a. EPA Chain-of-Custody Record

   b. Airbills

   c. EPA (SMO) Traffic Reports

   d. Sample Tags (if present) sealed in plastic bags.

4. All original receiving documents, including, but not limited to, the following documents:

   a. Form DC-1

   b. Other receiving forms or copies of receiving logbooks.

   c. SDG Cover Sheet

5. All original laboratory records of sample transfer, preparation, and analysis, including, but not limited to, the following documents:

   a. Original preparation and analysis forms or copies of preparation and analysis logbook pages.

   b. Internal sample and sample digestate/distillate transfer chain-of-custody records.

6. All other original case-specific documents in the possession of the laboratory, including, but not limited to, the following documents:

   a. Telephone contact logs.

   b. Copies of personal logbook pages.

   c. All handwritten case-specific notes.

   d. Any other case-specific documents not covered by the above.

   NOTE: All case-related documentation may be used or admitted as evidence in subsequent legal proceedings. Any other case-specific documents generated after the CSF is sent to EPA, as well as copies that are altered in any fashion, are also deliverables to EPA (original to the Region and copies to SMO and EMSL/LV).

   If the laboratory does submit case-specific documents to EPA after submission of the CSF, the documents should be numbered as an addendum to the CSF and a revised DC-2 form should be submitted; or the documents should be numbered as a new CSF and a new DC-2 form should be submitted to the Regions only.

G. Quarterly and Annual Verification of Instrument Parameters

The Contractor shall perform and report quarterly verification of instrument detection limits and linear range by the methods specified in Exhibit E for each instrument used under this contract. For the ICP instrumentation, the Contractor shall also perform and report annual interelement correction factors (including method of determination), wavelengths used and integration times. Forms for Quarterly and Annual Verification of Instrument Parameters for the current quarter and year shall be submitted in each SDG data package, using Forms X, XIA, XIB, and XII. Submission of Quarterly/Annual Verification of Instrument Parameters shall include the raw data used to determine those values reported.

H. Corrective Action Procedures

If a Contractor fails to adhere to the requirements detailed in this SOW, a Contractor may expect, but the Agency is not limited to the following actions: reduction of numbers of samples sent under this contract, suspension of sample shipment to the Contractor, data package audit, an on-site laboratory evaluation, remedial performance evaluation sample, and/or contract sanctions, such as a Cure Notice (see Exhibit E for additional details).

SECTION III

FORM INSTRUCTION GUIDE

This section contains specific instructions for the completion of all required Inorganic Data Reporting Forms. This section is organized into the following Parts:

A. General Information and Header Information

B. Cover Page -- Inorganic Analyses Data Package [COVER PAGE - IN]

C. Inorganic Analysis Data Sheet [FORM I - IN]

D. Initial and Continuing Calibration Verification [FORM II (PART 1) - IN]

E. CRDL Standard for AA and ICP [FORM II (PART 2) - IN]

F. Blanks [FORM III - IN]

G. ICP Interference Check Sample [FORM IV - IN]

H. Spike Sample Recovery [FORM V (PART 1) - IN]

I. Post Digest Spike Sample Recovery [FORM V (PART 2) - IN]

J. Duplicates [FORM VI - IN]

K. Laboratory Control Sample [FORM VII - IN]

L. Standard Addition Results [FORM VIII - IN]

M. ICP Serial Dilutions [FORM IX - IN]

N. Instrument Detection Limits (Quarterly) [FORM X - IN]

O. ICP Interelement Correction Factors (Annually) [FORM XI (PART 1) - IN]

P. ICP Interelement Correction Factors (Annually) [FORM XI (PART 2) - IN]

Q. ICP Linear Ranges (Quarterly) [FORM XII - IN]

R. Preparation Log [Form XIII - IN]

S. Analysis Run Log [Form XIV - IN]

T. Sample Log-In Sheet [Form DC-1]

U. Document Inventory Sheet [Form DC-2]

A. General Information and Header Information

The data reporting forms presented in Section IV in this Exhibit have been designed in conjunction with the computer-readable data format specified in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format. The specific length of each variable for computer-readable data transmission purposes is given in Exhibit H. Information entered on these forms must not exceed the size of the field given on the form, including such laboratory-generated items as Lab Name and Lab Sample ID.

Note that on the hardcopy forms (see Section IV), the space provided for entries is greater in some instances than the length prescribed for the variable as written to diskette (see Exhibit H). Greater space is provided on the hardcopy forms for the sake of visual clarity.

Values must be reported on the hardcopy forms according to the individual form instructions in this section. Each form submitted must be filled out completely for all analytes before proceeding to the next form of the same type. Do not submit multiple forms in place of one form if the information on those forms can be submitted on one form.

All characters which appear on the data reporting forms presented in the contract (Exhibit B, Section IV) must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the EPA Administrative Project Officer. The names of the various fields and analytes (i.e., "Lab Code," "Aluminum") must appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix (soil/water):" must appear, not just "Matrix").

All alphabetic entries made onto the forms by the Contractor must be in UPPERCASE letters (i.e., "LOW", not "Low" or "low"). If an entry does not fill the entire blank space provided on the form, null characters must be used to remove the remaining underscores that comprise the blank line. (See Exhibit H for additional instructions.) However, do not remove the underscores or vertical bar characters that delineate "boxes" on the forms.

Six pieces of information are common to the header sections of each data reporting form. These are: Lab Name, Contract, Lab Code, Case No., SAS No., and SDG No. This information must be entered on every form and must match on all forms.

The "Lab Name" must be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.

The "Contract" is the number of the EPA contract under which the analyses were performed.

The "Lab Code" is an alphabetic abbreviation of up to 6 characters, assigned by EPA, to identify the laboratory and aid in data processing. This lab code shall be assigned by EPA at the time a contract is awarded, and must not be modified by the Contractor, except at the direction of EPA.

The "Case No." is the EPA-assigned Case number (to 5 spaces) associated with the sample, and reported on the Traffic Report.

The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services. If samples are to be analyzed under SAS only, and reported on these forms, then enter SAS No. and leave Case No. blank. If samples are analyzed according to this SOW (Routine Analytical Services protocol) and have additional SAS requirements, list both Case No. and SAS No. on all forms. If the analyses have no SAS requirements, leave "SAS No." blank. (NOTE: Some samples in an SDG may have a SAS No., while others do not.)

The "SDG No." is the Sample Delivery Group (SDG) number. The SDG number is the EPA Sample Number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number must be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

The other information common to several of the forms is the "EPA Sample No.". This number appears either in the upper righthand corner of the form, or as the left column of a table summarizing data from a number of samples. When "EPA Sample No." is entered into the triple-spaced box in the upper righthand corner of a form, it must be centered on the middle line of the three lines that comprise the box.

All samples, matrix spikes and duplicates must be identified with an EPA Sample Number. For samples, matrix spikes and duplicates, the EPA Sample Number is the unique identifying number given in the Traffic Report that accompanied that sample.

In order to facilitate data assessment, the sample suffixes listed in Table 1 must be used.

Other pieces of information are common to many of the Data Reporting Forms. These include: Matrix and Level.

For "Matrix", enter "SOIL" for soil/sediment samples, and enter "WATER" for water samples. NOTE: The matrix must be spelled out. Abbreviations such as "S" or "W" must not be used.

For "Level", enter the determination of concentration level. Enter as "LOW" or "MED", not "L" or "M".

Note: All results must be transcribed to Forms II-XIV from the raw data to the specified number of decimal places that are described in Exhibits B and H. The raw data result is to be rounded only when the number of figures in the raw data result exceeds the maximum number of figures specified for that result entry for that form. If there are not enough figures in the raw data result to enter in the specified space for that result, then zeros must be used for decimal places to the specified number of reporting decimals for that result for a specific form. The following examples are provided:

Raw Data Result	Specified Format	Correct Entry on Form
95.99653	5.4 (to four decimal places)	95.9965
95.99653	5.3 (to three decimal places)	95.997
95.99653	5.2 (to two decimal places)	96.00
95.996	5.4 (to four decimal places)	95.9960
95.9	5.4 (to four decimal places)	95.9000

For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round up). If the figure following the last digit to be retained equals 5 and there are no digits to the right of the 5 or all digits to the right of the 5 equal zero, then round up if the digit to be retained is odd, or round down if that digit is even. See also Rounding Rules entry in Glossary (Exhibit G).

Before evaluating a number for being in control or out of control of a certain limit, the number evaluated must be rounded using EPA rounding rules to the significance reported for that limit. For instance, the control limit for an ICV is plus or minus 10% of the true value. A reported percent recovery value of 110.4 would be considered in control while a reported value of 110.6 would be considered out of control. In addition, a calculated value of 110.50 would be in control while a calculated value of 110.51 would be out of control.

B. Cover Page - Inorganic Analyses Data Package [COVER PAGE-IN]

This form is used to list all samples analyzed within a Sample Delivery Group, and to provide certain analytical information and general comments. It is also the document which is signed by the Laboratory Manager to authorize and release all data and deliverables associated with the SDG.

Complete the header information according to the instructions in Part A.

For samples analyzed using this SOW, enter " ILM02.0" for SOW No.

Enter the EPA Sample No. (including spikes and duplicates) (to seven spaces) of every sample analyzed within the SDG. Spikes must contain an "S" suffix and duplicates a "D" suffix. These sample numbers must be listed on the form in ascending alphanumeric order. Thus, if MAB123 is the lowest (considering both alpha and numeric characters) EPA Sample No. within the SDG, it would be entered in the first EPA Sample No. field. Samples would be listed below it, in ascending sequence - MAB124, MAB125, MAC111, MA1111, MA1111D, etc.

A maximum of twenty (20) sample numbers can be entered on this form. Submit additional Cover Pages, as appropriate, if the total number of samples, duplicates, and spikes in the SDG is greater than twenty (20).

A Lab Sample ID (to ten spaces) may be entered for each EPA Sample No. If a Lab Sample ID is entered, it must be entered identically (for each EPA Sample No.) on all associated data.

Enter "YES" or "NO" in answer to each of the two questions concerning ICP corrections. Each question must be explicitly answered with a "YES" or a "NO." The third question must be answered with a "YES" or "NO" if the answer to the second question is "YES." It should be left blank if the answer to the second question is "NO."

Under "Comments," enter any statements relevant to the analyses performed under the SDG as a whole.

Each Cover Page must be signed, in original, by the Laboratory Manager or the Manager's designee and dated, to authorize the release and verify the contents of all data and deliverables associated with an SDG.

C. Inorganic Analysis Data Sheet [FORM 1-IN]

This form is used to tabulate and report sample analysis results for target analytes (Exhibit C).

Complete the header information according to the instructions in Part A and as follows.

"Date Received" is the date (formatted MM/DD/YY) of sample receipt at the laboratory, as recorded on the Traffic Report, i.e., the Validated Time of Sample Receipt (VTSR).

"% Solids" is the percent of solids on a weight/weight basis in the sample as determined by drying the sample as specified in Exhibit D. Report percent solids to one decimal place (i.e., 5.3%). If the percent solids is not required because the sample is fully aqueous or less than 1% solids, then enter "0.0."

Enter the appropriate concentration units (UG/L for water or MG/KG dry weight for soil). Entering "MG/KG" means "mg/Kg dry weight" on this form.

Under the column labeled "Concentration," enter for each analyte either the value of the result (if the concentration is greater than or equal to the Instrument Detection Limit) or the Instrument Detection Limit for the analyte corrected for any dilutions (if the concentration is less than the Instrument Detection Limit). The concentration result must be reported to two significant figures if the result is less than 10; to three sig figures if the value is greater than or equal to 10.

Under the columns labeled "C," "Q," and "M," enter result qualifiers as identified below. If additional qualifiers are used, their explicit definitions must be included on the Cover Page in the Comments section.

FORM I-IN includes fields for three types of result qualifiers. These qualifiers must be completed as follows:

- C (Concentration) qualifier -- Enter "B" if the reported value was obtained from a reading that was less than the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL). If the analyte was analyzed for but not detected, a "U" must be entered.

- Q qualifier -- Specified entries and their meanings are as follows:

  E - The reported value is estimated because of the presence of interference. An explanatory note must be included under Comments on the Cover Page (if the problem applies to all samples) or on the specific FORM I-IN (if it is an isolated problem).

  M - Duplicate injection precision not met.

  N - Spiked sample recovery not within control limits.

  S - The reported value was determined by the Method of Standard Additions (MSA).

  W - Post-digestion spike for Furnace AA analysis is out of control limits (85-115%), while sample absorbance is less than 50% of spike absorbance. (See Exhibit E.)

  * - Duplicate analysis not within control limits.

  + - Correlation coefficient for the MSA is less than 0.995.

  Entering "S," "W," or "+" is mutually exclusive. No combination of these qualifiers can appear in the same field for an analyte.

- M (Method) qualifier -- Enter:

  - "P" for ICP
  - "A" for Flame AA
  - "F" for Furnace AA
  - "PM" for ICP when Microwave Digestion is used
  - "AM" for flame AA when Microwave Digestion is used
  - "FM" for Furnace AA when Microwave Digestion is used
  - "CV" for Manual Cold Vapor AA
  - "AV" for Automated Cold Vapor AA
  - "CA" for Midi-Distillation Spectrophotometric
  - "AS" for Semi-Automated Spectrophotometric
  - "C" for Manual Spectrophotometric
  - "T" for Titrimetric
  - " " where no data has been entered
  - "NR" if the analyte is not required to be analyzed.

A brief physical description of the sample, both before and after digestion, must be reported in the fields for color (before and after), clarity (before and after), texture and artifacts. For water samples, report color and clarity. For soil samples, report color, texture and artifacts.

The following descriptive terms are recommended:

Color	-	red, blue, yellow, green, orange, violet, white, colorless, brown, grey, black
Clarity	-	clear, cloudy, opaque
Texture	-	fine (powdery), medium (sand), coarse (large crystals or rocks)

If artifacts are present, enter "YES" in the artifacts field and describe the artifacts in the Comments field. If artifacts are not present, leave this field blank.

Note any significant changes that occur during sample preparation (i.e., emulsion formation) in the Comments field. Enter any sample-specific comments concerning the analyte results in the Comments field.

D. Initial and Continuing Calibration Verification [FORM II(PART 1)-IN]

This form is used to report analyte recoveries from calibration solutions.

Complete the header information according to the instructions in Part A and as follows.

Enter the Initial Calibration Source (12 spaces maximum) and the Continuing Calibration Source (12 spaces maximum). Enter "EPA-LV" or "EPA-CI" to indicate EPA EMSL Las Vegas or Cincinnati, respectively, as the source of EPA standards. When additional EPA supplied solutions are prepared in the future, the Contractor must use the codes supplied with those solutions for identification. If other sources were used, enter sufficient information in the available 12 spaces to identify the manufacturer and the solution used.

Use additional FORMs II(PART 1)-IN if more calibration sources were used.

Under "Initial Calibration True," enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Initial Calibration Verification Solution.

Under "Initial Calibration Found," enter the most recent value (in ug/L, to two decimal places), of the concentration of each analyte measured in the Initial Calibration Verification Solution.

Under "Initial Calibration %R," enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Found(ICV)}}{\text{True(ICV)}} \times 100 \qquad (2.1)$$

Where, True(ICV) is the true concentration of the analyte in the Initial Calibration Verification Solution and Found(ICV) is the found concentration of the analyte in the Initial Calibration Verification Solution.

The values used in equation 2.1 for True(ICV) and Found(ICV) must be exactly those reported on this form.

Under "Continuing Calibration True," enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Continuing Calibration Verification Solution.

Under "Continuing Calibration Found," enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the Continuing Calibration Verification Solution.

Note that the form contains two "Continuing Calibration Found" columns. The column to the left must contain values for the first Continuing Calibration Verification, and the column to the right must contain values for the second Continuing Calibration Verification. The column to the right should be left blank if no second Continuing Calibration Verification was performed.

If more than one FORM II(PART 1)-IN is required to report multiple Continuing Calibration Verifications, then the column to the left on the second form must contain values for the third Continuing Calibration Verification, the column to the right must contain values for the fourth Continuing Calibration Verification, and so on.

Under "Continuing Calibration %R," enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Found(CCV)}}{\text{True(CCV)}} \times 100 \qquad (2.2)$$

where, True(CCV) is the true concentration of each analyte, and Found(CCV) is the found concentration of the analyte in the Continuing Calibration Verification Solution.

The values used in equation 2.2 for True(CCV) and Found(CCV) must be exactly those reported on this form.

Note that the form contains two "Continuing Calibration %R" columns. Entries to these columns must follow the sequence detailed above for entries to the "Continuing Calibration Found" columns.

Under "M," enter the method used or "NR," as explained in Part C.

If more than one wavelength is used to analyze an analyte, submit additional FORMs II(PART 1)-IN as appropriate.

The order of reporting ICVs and CCVs for each analyte must follow the temporal order in which the standards were run starting with the first Form IIA and moving from the left to the right continuing to the following Form IIA's as appropriate. For instance, the first ICV for all analytes must be reported on the first Form IIA. In a run where three CCVs were analyzed, the first CCV must be reported in the left CCV column on the first Form IIA and the second CCV must be reported in the right column of the same form. The third CCV must be reported in the left CCV column of the second Form IIA. On the second Form IIA, the ICV column and the right CCV column must be left empty in this example. In the previous example, if a second run for an analyte was needed, the ICV of that run must be reported on a third Form IIA and the CCVs follow in the same fashion as explained before. In the case where two wavelengths are use used for an analyte, all ICV and CCV results of one wavelength from all runs must be reported before proceeding to report the results of the second wavelength used.

E. CRDL Standard for AA and ICP [FORM II(PART 2)-IN]

This form is used to report analyte recoveries from analyses of the CRDL Standards for AA (CRA) and 2x the CRDL Standards for ICP (CRI).

Complete the header information according to the instructions in Part A and as follows.

Enter the AA CRDL Standard Source (12 spaces maximum) and the ICP CRDL Standard Source (12 spaces maximum), as explained in Part D.

Under "CRDL Standard for AA True," enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the CRDL Standard Source Solution that was analyzed.

Under "CRDL Standard for AA Found," enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the CRDL Standard Solution.

Under "CRDL Standard for AA %R," enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Found CRDL Standard for AA}}{\text{True CRDL Standard for AA}} \times 100 \quad (2.3)$$

Under "CRDL Standard for ICP Initial True," enter the value (to one decimal place) of the concentration of each analyte in the CRDL Standard Solution that was analyzed by ICP for analytical samples associated with the SDG. Concentration units are ug/L.

Under "CRDL Standard for ICP Initial Found," enter the value (to two decimal places) of the concentration of each analyte measured in the CRDL Standard Solution analyzed at the beginning of each run. Concentration units are ug/L.

Under "CRDL Standard for ICP, Initial %R," enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{CRDL Standard for ICP Initial Found}}{\text{CRDL Standard for ICP True}} \times 100 \quad (2.4)$$

Under "CRDL Standard for ICP Final Found," enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the CRDL Standard Solution analyzed at the end of each run.

Under "CRDL Standard for ICP Final %R," enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{CRDL Standard for ICP Final Found}}{\text{CRDL Standard for ICP True}} \times 100 \quad (2.5)$$

All %R values reported in equations 2.3, 2.4, and 2.5 must be calculated using the exact true and found values reported on this form.

Note that for every initial solution reported there must be a final one. However, the opposite is not true. If a CRDL Standard for ICP (CRI) was required to be analyzed in the middle of a run (to avoid exceeding the 8-hour limit), it must be reported in the "Final Found" section of this form.

If more CRI or CRA analyses were required or analyses were performed using more than one wavelength per analyte, submit additional FORMs II(PART 2)-IN as appropriate.

The order of reporting CRAs and CRIs for each analyte must follow the temporal order in which the standards were run starting with the first Form IIB and continuing to the following Form IIBs as appropriate. The order of reporting CRA and CRI is independent with respect to each other. When multiple wavelengths are used for one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

F. Blanks [FORM III-IN]

This form is used to report analyte concentrations found in the Initial Calibration Blank (ICB), in Continuing Calibration Blanks (CCB), and in the Preparation Blank (PB).

Complete the header information according to the instructions in Part A and as follows.

Enter "SOIL" or "WATER" as appropriate as the matrix of the Preparation Blank. No abbreviations or other matrix descriptors may be used.

According to the matrix specified for the Preparation Blank, enter "UG/L" (for water) or "MG/KG" (for soil) as the Preparation Blank concentration units.

Under "Initial Calib. Blank," enter the concentration (in ug/L, to one decimal place) of each analyte in the most recent Initial Calibration Blank.

Under the "C" qualifier field, for any analyte enter "B" if the absolute value of the analyte concentration is less than the CRDL but greater than or equal to the IDL. Enter "U" if the absolute value of the analyte in the blank is less than the IDL.

Under "Continuing Calibration Blank 1," enter the concentration (in ug/L, to one decimal place) of each analyte detected in the first required Continuing Calibration Blank (CCB) analyzed after the Initial Calibration Blank. Enter any appropriate qualifier, as explained for the "Initial Calibration Blank," to the "C" qualifier column immediately following the "Continuing Calibration Blank 1" column.

If only one Continuing Calibration Blank was analyzed, then leave the columns labeled "2" and "3" blank. If up to three CCBs were analyzed, complete the columns labeled "2" and "3," in accordance with the instructions for the "Continuing Calibration Blank 1" column. If more than three Continuing Calibration Blanks were analyzed, then complete additional FORMs III-IN as appropriate.

Under "Preparation Blank," enter the concentration in ug/L (to three decimal places) for a water blank or in mg/Kg (to three decimal places) for a soil blank, of each analyte in the Preparation Blank. Enter any appropriate qualifier, as explained for the "Initial Calibration Blank," to the "C" qualifier column immediately following the "Preparation Blank" column.

For all blanks, enter the concentration of each analyte (positive or negative) measured above the IDL or below the negative value of the IDL.

Under "M," enter the method used, as explained in Part C.

If more than one wavelength is used to analyze an analyte, submit additional FORMs III-IN as appropriate.

The order of reporting ICBs and CCBs for each analyte must follow the temporal order in which the blanks were run starting with the first Form III and moving from left to right and continuing to the following Form IIIs as explained in Part D. When multiple wavelengths are used for the analysis of one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

G. ICP Interference Check Sample [FORM IV-IN]

This form is used to report Interference Check Sample (ICS) results for each ICP instrument used in Sample Delivery Group analyses.

Complete the header information according to the instructions in Part A and as follows:

For "ICP ID Number," enter an identifier that uniquely identifies a specific instrument within the Contractor laboratory. No two ICP instruments within a laboratory may have the same ICP ID Number.

Enter "ICS Source" (12 spaces maximum) as explained in Part D. For EPA solutions, include in the source name a number identifying it (e.g., EPA-LV87).

Under "True Sol. A," enter the true concentration (in ug/L, to the nearest whole number) of each analyte present in Solution A.

Under "True Sol. AB," enter the true concentration (in ug/L, to the nearest whole number) of each analyte present in Solution AB.

Under "Initial Found Sol. A," enter the concentration (in ug/L, to the nearest whole number) of each analyte found in the initial analysis of Solution A as required in Exhibit E.

Under "Initial Found Sol. AB," enter the concentration (in ug/L, to one decimal place) of each analyte in the initial analysis of Solution AB as required in Exhibit E.

Under "Initial Found %R," enter the value (to one decimal place) of the percent recovery computed for true solution AB greater than zero according to the following equation:

$$\%R = \frac{\text{Initial Found Solution AB}}{\text{True Solution AB}} \times 100 \qquad (2.6)$$

Leave the field blank if true solution AB equals zero.

Under "Final Found Sol. A," enter the concentration (in ug/L, to the nearest whole number) of each analyte found in the final analysis of Solution A as required in Exhibit E.

Under "Final Found Sol. AB," enter the concentration (in ug/L, to one decimal place) of each analyte found in the final analysis of Solution AB as required in Exhibit E.

For All Found values of solutions A and AB, enter the concentration (positive, negative, or zero) of each analyte at each wavelength used for analysis by ICP.

Under "Final Found %R," enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Final Found Solution AB}}{\text{True Solution AB}} \times 100 \qquad (2.7)$$

All %R values reported must be calculated using the exact true and found values reported on this form.

Note that for every initial solution reported there must be a final one. However, the opposite is not true. If an ICS was required to be analyzed in the middle of a run (to avoid exceeding the 8-hour limit), it must be reported in the "Final Found" section of this form.

If more ICS analyses were required, submit additional FORMs IV-IN as appropriate.

The order of reporting ICSs for each analyte must follow the temporal order in which the standards were run starting with the first Form IV and continuing to the following Form IVs as appropriate. When multiple wavelengths are used for one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

H. Spike Sample Recovery [FORM V(PART 1)-IN]

This form is used to report results for the pre-digest spike.

Complete the header information according to the instructions in Part A and as follows.

Indicate the appropriate matrix, level and concentration units (ug/L for water and mg/Kg dry weight for soil) as explained in Parts A and C.

For "%Solids for Sample," enter the percent solids (as explained in Part C) for the original sample of the EPA Sample Number reported on the form. Note that this number must equal the one reported on Form I for that sample.

In the "EPA Sample No." box, enter the EPA Sample Number (7 places maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box.

Under "Control Limit %R," enter "75-125" if the spike added value was greater than or equal to one-fourth of the sample result value. If not, leave the field empty.

Under "Spiked Sample Result (SSR)," enter the measured value (to four decimal places), in appropriate units, for each relevant analyte in the matrix spike sample. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

Under "Sample Result (SR)," enter the measured value (to four decimal places) for each required analyte in the sample (reported in the EPA Sample No. box) on which the matrix spike was performed. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

Under "Spike Added (SA)," enter the value (to two decimal places) for the concentration of each analyte added to the sample. The same concentration units must be used for spiked sample results, unspiked (original sample) results, and spike added sample results. If the "spike added" concentration is specified in the contract, the value added and reported must be that specific concentration in appropriate units, corrected for spiked sample weight and % solids (soils) or spiked sample volume (waters).

Under "%R," enter the value (to one decimal place) of the percent recovery for all spiked analytes computed according to the following equation:

$$\%R = \frac{(SSR - SR)}{SA} \times 100 \qquad (2.8)$$

%R must be reported, whether it is negative, positive or zero.

The values for SSR, SR, and SA must be exactly those reported on this form. A value of zero must be used in calculations for SSR or SR if the analyte value is less than the IDL.

Under "Q," enter "N" if the Spike Recovery (%R) is out of the control limits (75-125) and the Spike Added (SA) is greater than or equal to one-fourth of the Sample Result (SR).

Under "M," enter the method used (as explained in Part C) or enter "NR" if the analyte is not required in the spike.

If different samples were used for spike sample analysis of different analytes, additional FORMs V(PART 1)-IN must be submitted for each sample as appropriate.

I. Post Digest Spike Sample Recovery [FORM V(PART 2)-IN]

This form is used to report results for the post-digest spike recovery which is based upon the addition of a known quantity of analyte to an aliquot of the digested sample.

Complete the header information according to the instructions in Part A and as follows.

In the "EPA Sample No." box, enter the EPA Sample Number (7 spaces maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box.

The "Control Limit %R" and "Q" fields must be left blank until limits are established by EPA. At that time, the Contractor will be informed how to complete these fields.

Under "Spiked Sample Result (SSR)," enter the measured value (in ug/L, to two decimal places) for each analyte in the post-digest spike sample. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

Under "Sample Result (SR)," enter the measured value (in ug/L, to two decimal places) for the concentration of each analyte in the sample (reported in the EPA Sample No. box) on which the spike was performed. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

Under "Spike Added (SA)," enter the value (in ug/L, to one decimal place) for each analyte added to the sample. The same concentration units must be used for spiked sample results, unspiked (original sample) results, and spike added sample results. If the spike added concentration is specified in the contract, the value added and reported must be that specific concentration in appropriate units.

Under "%R," enter the value (to one decimal place) of the percent recovery for all spiked analytes computed according to Equation 2.8 in Part H

%R must be reported, whether it is negative, positive or zero.

The values for SSR, SR, and SA must be exactly those reported on this form. A value of zero must be substituted for SSR or SR if the analyte value is less than the IDL.

Under "M," enter the method used as explained in Part C, or enter "NR" if the spike was not required.

If different samples were used for spike sample analysis of different analytes, additional FORMS V(PART 1)-IN must be submitted.

J. Duplicates [FORM VI-IN]

The duplicates form is used to report results of duplicate analyses. Duplicate analyses are required for % solids values and all analyte results.

Complete the header information according to the instructions in Part A and as follows.

Indicate the appropriate matrix, level and concentration units (ug/L for water and mg/Kg dry weight for soil) as explained in Parts A and C.

For "% Solids for Sample," enter the percent solids (as explained in Part C) for the original sample of the EPA Sample Number reported on the form. Note that this number must equal the one reported on Form I for that sample.

For "% Solids for Duplicate," enter the percent solids (as explained in Part C) for the duplicate sample of the EPA Sample Number reported on the form.

In the "EPA Sample No." box, enter the EPA Sample Number (7 spaces maximum) of the sample from which the duplicate sample results on this form were obtained. The number must be centered in the box.

Under "Control Limit," enter the CRDL (in appropriate units, ug/L for water or mg/kg dry weight basis compared to the original sample weight and percent solids) for the analyte if the sample or duplicate values were less than 5x CRDL and greater than or equal to the CRDL. If the sample and duplicate values were greater than or equal to 5x CRDL, leave the field empty.

Under Sample (S), enter the original measured value (to four decimal places) for the concentration of each analyte in the sample (reported in the EPA Sample No. box) on which a Duplicate analysis was performed. Concentration units are those specified on the form. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample (S)" column.

Under Duplicate (D), enter the measured value (to four decimal places) for each analyte in the Duplicate sample. Concentration units are those specified on the form. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Duplicate (D)" column.

For solid samples, the concentration of the original sample must be computed using the weight and % solids of the original sample. The concentration of the duplicate sample must be computed using the weight of the duplicate sample, but the % solids of the original sample.

Under RPD, enter the absolute value (to one decimal place) of the Relative Percent Difference for all analytes detected above the IDL in either the sample or the duplicate, computed according to the following equation:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad (2.9)$$

The values for S and D must be exactly those reported on this form. A value of zero must be substituted for S or D if the analyte concentration is less than the IDL in either one. If the analyte concentration is less than the IDL in both S and D, leave the RPD field empty.

Under "Q," enter "*" if the duplicate analysis for the analyte is out of control. If both sample and duplicate values are greater than or equal to 5x CRDL, then the RPD must be less than or equal to 20% to be in control. If either sample or duplicate values are less than 5x CRDL, then the absolute difference between the two values must be less than the CRDL to be in control. If both values are below the CRDL, then no control limit is applicable.

Under "M," enter method used as explained in Part C.

K. Laboratory Control Sample [FORM VII-IN]

This form is used to report results for the solid and aqueous Laboratory Control Samples.

Complete the header information according to the instructions in Part A and as follows.

For the Solid LCS Source (12 spaces maximum), enter the appropriate EPA sample number if the EPA provided standard was used. Substitute an appropriate number provided by the EPA for LCS solutions prepared in the future. If other sources were used, identify the source as explained in Part D. For the Aqueous LCS Source, enter the source name (12 spaces maximum) as explained in Part D.

Under "Aqueous True," enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Aqueous LCS Standard Source.

Under "Aqueous Found," enter the measured concentration (in ug/L, to two decimal places) of each analyte found in the Aqueous LCS solution.

Under "Aqueous %R," enter the value of the percent recovery (to one decimal place) computed according to the following equation:

$$\%R = \frac{\text{Aqueous LCS Found}}{\text{Aqueous LCS True}} \times 100 \qquad (2.10)$$

Under "Solid True," enter the value (in mg/Kg, to one decimal place) of the concentration of each analyte in the Solid LCS Source.

Under "Solid Found," enter the measured value (in mg/Kg, to one decimal place) of each analyte found in the Solid LCS solution.

Under "C," enter "B" or "U" or leave empty, to describe the found value of the solid LCS as explained in Part C.

Under "Limits," enter the lower limit (in mg/Kg, to one decimal place) in the left column, and the upper limit (in mg/Kg, to one decimal place) in the right column, for each analyte in the Solid LCS Source solution.

Under "Solid %R," enter the value of the percent recovery (to one decimal place) computed according to the following equation:

$$\%R = \frac{\text{Solid LCS Found}}{\text{Solid LCS True}} \times 100 \qquad (2.11)$$

The values for true and found aqueous and solid LCSs used in equations 2.10 and 2.11 must be exactly those reported on this form. If the analyte concentration is less than the IDL, a value of zero must be substituted for the solid LCS found.

Submit additional FORMs VII-IN as appropriate, if more than one aqueous LCS or solid LCS was required.

L. Standard Addition Results [FORM VIII-IN]

This form is used to report the results of samples analyzed using the Method of Standard Additions (MSA) for Furnace AA analysis.

Complete the header information according to the instructions in Part A.

Under "EPA Sample No.," enter the EPA Sample Numbers (7 spaces maximum) of all analytical samples analyzed using the MSA. This includes reruns by MSA (if the first MSA was out of control) as explained in Exhibit E.

Note that only field samples and duplicates may be reported on this form, thus the EPA Sample Number usually has no suffix or a "D."

A maximum of 32 samples can be entered on this form. If additional samples required MSA, submit additional FORMs VIII-IN. Samples must be listed in alphanumeric order per analyte, continuing to the next FORM VIII-IN if applicable.

Under "An," enter the chemical symbol (2 spaces maximum) for each analyte for which MSA was required for each sample listed. The analytes must be in alphabetic listing of the chemical symbols.

Results for different samples for each analyte must be reported sequentially, with the analytes ordered according to the alphabetic listing of their chemical symbols. For instance, results for As (arsenic) in samples MAA110, MAA111, and MAA112 would be reported in sequence, followed by the result for Pb (lead) in MAA110 etc.

Under "0 ADD ABS," enter the measured value in absorbance units (to three decimal places) for the analyte before any addition is performed.

Under "1 ADD CON," enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the first addition to the sample analyzed by MSA.

Under "1 ADD ABS," enter the measured value (in the same units and decimal places as "0 ADD ABS") of the sample solution spiked with the first addition.

Under "2 ADD CON," enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the second addition to the sample analyzed by MSA.

Under "2 ADD ABS," enter the measured value (in the same units and decimal places as "0 ADD ABS") of the sample solution spiked with the second addition.

Under "3 ADD CON," enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the third addition to the sample analyzed by MSA.

Under "3 ADD ABS," enter the measured value (in the same units and decimal places as "0 ADD ABS") of the sample solution spiked with the third addition.

Note that "0 ADD ABS," "1 ADD ABS" "2 ADD ABS," and "3 ADD ABS" must have the same dilution factor.

Under "Final Conc.," enter the final analyte concentration (in ug/L, to one decimal place) in the sample as determined by MSA computed according to the following formula:

Final Conc. = - (x-intercept) (2.12)

Note that the final concentration of an analyte does not have to equal the value for that analyte which is reported on FORM I-IN for that sample.

Under "r," enter the correlation coefficient (to four decimal places) that is obtained for the least squares regression line representing the following points (x,y):(0.0, "0 ADD ABS"), ("1 ADD CON," "1 ADD ABS"), ("2 ADD CON," "2 ADD ABS"), ("3 ADD CON," "3 ADD ABS").

Note that the correlation coefficient must be calculated using the ordinary least squares linear regression (unweighted) according to the following formula:

$$r = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{[N \sum x_i^2 - (\sum x_i)^2]^{1/2} [N \sum y_i^2 - (\sum y_i)^2]^{1/2}} \quad (2.13)$$

Under "Q," enter "+" if r is less than 0.995. If r is greater than or equal to 0.995, then leave the field empty.

M. ICP Serial Dilutions [FORM IX-IN]

This form is used to report results for ICP serial dilution.

Complete the header information according to the instructions in Part A and as follows.

In the "EPA Sample No." box, enter the EPA Sample Number (7 places maximum) of the sample for which serial dilution analysis results on this form were obtained. The number must be centered in the box.

Under "Initial Sample Result (I)," enter the measured value (in ug/L, to two decimal places) for each ICP analyte in the undiluted sample (for the EPA sample number reported on this form). Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Initial Sample Result (I)" column.

Note that the Initial Sample Concentration for an analyte does not have to equal the value for that analyte reported on FORM I-IN for that sample. It is the value of the analyte concentration (uncorrected for dilution) that is within the linear range of the instrument.

Under "Serial Dilution Result (S)", enter the measured concentration value (in ug/L, to two decimal places) for each ICP analyte in the diluted sample. The value must be adjusted for that dilution. Enter any appropriate qualifier, as explained in Part B, to the "C" qualifier column immediately following the "Serial Dilution Result (S)" column.

Note that the Serial Dilution Result (S) is obtained by multiplying by five the instrument measured value (in ug/L) of the serially diluted sample and that the "C" qualifier for the serial dilution must be established based on the serial dilution result before correcting it for the dilution regardless of the value reported on the form.

Under "% Difference," enter the absolute value (to one decimal place) of the percent difference in concentration of required analytes, between the original sample and the diluted sample (adjusted for dilution) according to the following formula:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100 \qquad (2.14)$$

The values for I and S used to calculate % Difference in equation 2.14 must be exactly those reported on this form. A value of zero must be substituted for S if the analyte concentration is less than the IDL. If the analyte concentration in (I) is less than the IDL, concentration leave "% Difference" field empty.

Under "Q," enter "E" if the % Difference is greater than 10% and the original sample concentration (reported on FORM I-IN) is greater than 50x the IDL reported on FORM X-IN.

Under "M," enter the method of analysis for each analyte as explained in Part C.

N. Instrument Detection Limits (Quarterly) [FORM X-IN]

This form documents the Instrument Detection Limits for each instrument that the laboratory used to obtain data for the Sample Delivery Group. Only the instrument and wavelengths used to generate data for the SDG must be included.

Although the Instrument Detection Limits (IDLs) are determined quarterly (every three calendar months) a copy of the quarterly instrument detection limits must be included with each SDG data package on FORM(s) X-IN.

Complete the header information according to the instructions in Part A and as follows.

Enter the date (formatted MM/DD/YY) on which the IDL values were obtained (or became effective).

Enter ICP ID Number, Flame AA ID Number, and Furnace AA ID Number (12 spaces maximum each). These ID Numbers are used to uniquely identify each instrument that the laboratory uses to do CLP work.

Enter the Mercury instrument ID number in the Flame AA ID Number field.

Under "Wavelength," enter the wavelength in nanometers (to two decimal places) for each analyte for which an Instrument Detection Limit (IDL) has been established and is listed in the IDL column. If more than one wavelength is used for an analyte, use other FORMs X-IN as appropriate to report the Instrument Detection Limit.

Under "Background," enter the type of background correction used to obtain Furnace AA data. Enter "BS" for Smith Hieftje, "BD" for Deuterium Arc, or "BZ" for Zeeman background correction.

Contract Required Detection Limits (in ug/L) as established in Exhibit C, must appear in the column headed "CRDL."

Under "IDL," enter the Instrument Detection Limit (ug/L, to one decimal place) as determined by the laboratory for each analyte analyzed by the instrument for which the ID Number is listed on this form. The IDL results must be reported to two significant figures if the result value is less than 10, and to three significant figures if the value is greater than or equal to 10. When calculating IDL values, always round up to the appropriate significant figure. This deviation from the EPA rounding rule is necessary to prevent the reporting of detected values for results that fall in the noise region of the calibration curve.

Under "M," enter the method of analysis used to determine the instrument detection limit for each wavelength used. Use appropriate codes as explained in Part C.

Use additional FORMs X-IN if more instruments and wavelengths are used. Note that the date on this form must not exceed the analysis dates in the SDG data package or precede them by more than three months.

Use the Comments section to indicate alternative wavelengths and the conditions under which they are used.

O. ICP Interelement Correction Factors (Annually) [FORM XI(PART 1)-IN]

This form documents for each ICP instrument the interelement correction factors applied by the Contractor laboratory to obtain data for the Sample Delivery Group.

Although the correction factors are determined annually (every twelve calendar months), a copy of the results of the annual interelement correction factors must be included with each SDG data package on FORM XI(PART 1)-IN.

Complete the header information according to instructions in Part A and as follows.

Enter the ICP ID Number (12 spaces maximum), which is a unique number designated by the laboratory to identify each ICP instrument used to produce data in the SDG package. If more than one ICP instrument is used, submit additional FORMs XI(PART 1)-IN as appropriate.

Report the date (formatted as MM/DD/YY) on which these correction factors were determined for use. This date must not exceed the ICP analysis dates in the SDG data package or precede them by more than twelve calendar months.

Under "Wavelength," list the wavelength in nanometers (to two decimal places) used for each ICP analyte. If more than one wavelength is used, submit additional FORMs XI(PART 1)-IN as appropriate.

Under "Al," "Ca," "Fe," "Mg, enter the correction factor (negative, positive or zero, to seven decimal places, 10 spaces maximum) for each ICP analyte. If correction factors for another analyte are applied, use the empty column and list the analyte's chemical symbol in the blank two-space header field provided for that column.

If corrections are not applied for an analyte, a zero must be entered for that analyte to indicate that the corrections were determined to be zero. If correction factors are applied for more than one additional analyte, use FORM XI(PART 2)-IN.

P. ICP Interelement Correction Factors (Annually) [FORM XI(PART 2)-IN]

This form is used if correction factors for analytes other than Al, Ca, Fe, Mg, and one more analyte of the Contractor's choice, were applied to the analytes analyzed by ICP. Complete this form as for FORM XI(PART 1)-IN by listing the chemical symbol for additional analytes in the heading of the empty columns in the two-space fields provided.

Columns of correction factors for additional analytes must be entered left to right starting on FORM XI(PART 1)-IN and proceeding to FORM XI(PART 2)-IN, according to the alphabetic order of their chemical symbols. Note that correction factors for Al, Ca, Fe, and Mg are all required and are to be listed first (as they appear on FORM XI(PART 1)-IN).

Q. ICP Linear Ranges (Quarterly) [FORM XII-IN]

This form documents the quarterly linear range analysis for each ICP instrument that the laboratory used to obtain data for the SDG.

Complete the header information according to the instructions in Part A and as follows.

Enter the ICP ID Number (12 spaces maximum), which is a unique number designated by the Contractor to identify each ICP instrument used to produce data for the SDG. If more than one ICP instrument is used, submit additional FORMs XII-IN as appropriate.

Report the date (formatted as MM/DD/YY) on which these linear ranges were determined for use. This date must not exceed the dates of analysis by ICP in the SDG data package and must not precede the analysis dates by more than three calendar months.

Under "Integ. Time (Sec.)," enter the integration time (in seconds to two decimal places) used for each measurement taken from the ICP instrument.

Under "Concentration," enter the concentration (in ug/L) that is the upper limit of the ICP instrument linear range as determined in Exhibit E. Any measurement in the SDG data package at or below this concentration is within the linear range. Any measurement above it is out of the linear range, and thus, is an estimated value and must be diluted into the linear range.

Under "M," enter the method of analysis for each analyte as explained in Part C.

If more instruments or analyte wavelengths are used, submit additional FORMs XII-IN as appropriate.

R. Preparation Log [Form XIII-IN]

This Form is used to report the preparation run log.

All field samples and all quality control preparations (including duplicates, matrix spikes, LCSs, PBs and repreparations) associated with the SDG must be reported on Form XIII.

Submit one Form XIII per batch, per method, if no more than thirty-two preparations, including quality control preparations, were performed. If more than thirty-two preparations per batch, per method, were performed, then submit additional copies of Form XIII as appropriate. Submit a separate Form XIII for each batch.

The order in which the Preparation Logs are submitted is very important. Form XIII must be organized by method, by batch. Later batches within a method must follow earlier ones. Each batch must start on a separate Form XIII.

Complete the header information according to the instructions in Part A, and as follows:

For "Method," enter the method of analysis (two characters maximum) for which the preparations listed on the Form were made. Use appropriate method codes as specified in Part C.

Under "EPA Sample No.," enter the EPA Sample Number of each sample in the SDG, and of all other preparations such as duplicates, matrix spikes, LCSs, PBs, and repreparations (all formatted according to Table 1). All EPA Sample Numbers must be listed in ascending alphanumeric order, continuing to the next Form XIII if applicable.

Under "Preparation Date," enter the date (formatted MM/DD/YY) on which each sample was prepared for analysis by the method indicated in the header section of the Form.

Note that the date never changes on a single Form XIII because the form must be submitted per batch.

Under "Weight," enter the wet weight (in grams, to two decimal places) of each soil sample prepared for analysis by the method indicated in the header section of the Form. If the sample matrix is water, then leave the field empty.

Under "Volume," enter the final volume (in mL, to the nearest whole number) of the preparation for each sample prepared for analysis by the method indicated in the header section of the Form. This field must have a value for each sample listed.

S. Analysis Run Log [Form XIV-IN]

This Form is used to report the sample analysis run log.

A run is defined as the totality of analyses performed by an instrument throughout the sequence initiated by, and including, the first SOW-required calibration standard and terminated by, and including, the continuing calibration verification and blank following the last SOW-required analytical sample.

All field samples and all quality control analyses (including calibration standards, ICVs, CCVs, ICBs, CCBs, CRAs, CRIs, ICSs, LRSs, LCSs, PBs, duplicates, serial dilutions, pre-digestion spikes, post-digestion spikes, analytical spikes, and each addition analyzed for the method of standard addition determination) associated with the SDG must be reported on Form XIV. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

Submit one Form XIV per run if no more than thirty-two (32) analyses, including instrument calibration, were analyzed in the run. If more than thirty-two analyses were performed in the run, submit additional Forms XIV as appropriate.

The order in which the Analysis Run Logs are submitted is very important. Form XIV must be organized by method, by run. Later runs within a method must follow earlier ones. Each analytical run must start on a separate Form XIV. Therefore, instrument calibration must be the first entry on the form for each new run. In addition, the run is considered to have ended if it is interrupted for any reason, including termination for failing QC parameters.

Complete the header information according to the instructions in Part A, and as follows:

For "Instrument ID Number," enter the instrument ID number, (12 spaces maximum), which must be an identifier designated by the laboratory to uniquely identify each instrument used to produce data which are required to be reported in the SDG deliverable. If more than one instrument is used, submit additional Forms XIV as appropriate.

For "Method," enter the method code (two characters maximum) according to the specifications in Part C.

For "Start Date," enter the date (formatted MM/DD/YY) on which the analysis run was started.

For "End Date," Enter the date (formatted MM/DD/YY) on which the analysis run was ended.

Under "EPA Sample No.," enter the EPA sample number of each analysis, including all QC operations applicable to the SDG (formatted according to Table 1). All EPA Sample Numbers must be listed in increasing temporal (date and time) order of analysis, continuing to the next Form XIV for the instrument run if applicable. The analysis date and time of other analyses not associated with the SDG, but analyzed by the instrument in the reported analytical run, must be reported. Those analyses must be identified with the EPA Sample No. of "ZZZZZZ."

Under "D/F," enter the dilution factor (to two decimal places) by which the final digestate or distillate needed to be diluted for each analysis to be performed. The dilution factor does not include the dilution inherent in the preparation as specified by the preparation procedures in Exhibit D.

The dilution factor is required for all entries on Form XIV.

Note that for a particular sample a dilution factor of "1" must be entered if the digestate or distillate were analyzed without adding any further volume of dilutant or any other solutions to the "Volume" or an aliquot of the "Volume" listed on Form XIII for that sample.

For EPA supplied solutions such as ICVs, ICSs, and LCSs, a dilution factor must be entered if the supplied solution had to be diluted to a dilution different from that specified by the instructions provided with the solution. The dilution factor reported in such a case must be that which would make the reported true values on the appropriate form for the solution equal those that were supplied with the solution by the EPA. For instance, ICV-2(0887) has a true value of 104.0 ug/L at a 20 fold dilution. If the solution is prepared at a 40 fold dilution, a dilution factor of "2" must be entered on Form XIV and the uncorrected instrument reading is compared to a true value of 52 ug/L. In this example, Form II will have a true value of 104.0 regardless of the dilution used. The found value for the ICV must be corrected for the dilution listed on Form XIV using the following formula:

Found value on Form II = Instrument readout in ug/L x D/F

Under "Time," enter the time, (in military format - HHMM), at which each analysis was performed. If an auto sampler is used with equal analysis time and intervals between analyses, then only the start time of the run (the time of analysis of the first calibration standard) and end time of the run (the time of analysis of the final CCV or CCB, which ever is later) need to be reported.

Under "% R," enter the percent recovery (to one decimal place) for each Furnace AA analytical spike analyzed. If the analytical spike was performed on more than one analyte, use additional Forms XIV as appropriate. Leave the "% R" field empty if the analysis reported is not for an analytical spike. %R must be recorded even if the result is not used.

A %R value of "-9999.9" must be entered for the analytical spike if either the sample or analytical results is greater than the calibration range of the instrument.

Under "Analytes," enter "X" in the column of the designated analyte to indicate that the analyte value was used from the reported analysis to report data in the SDG. Leave the column empty for each analyte if the analysis was not used to report the particular analyte.

Entering "X" appropriately is very important. The "X" is used to link the samples with their related QC. It also links the dilution factor with the appropriate result reported on Forms I-IX. For each analyte result reported on any of the Forms I-IX, there must be one, and only one, properly identified entry on Form XIV for which an "X" is entered in the column for that analyte.

T. Sample Log-In Sheet [Form DC-1]

This form is used to document the receipt and inspection of samples and containers. One original of Form DC-1 is required for each sample shipping container, e.g., cooler. If the samples in a single sample shipping container must be assigned to more than one Sample Delivery Group, the original Form DC-1 shall be placed with the deliverables for the Sample Delivery Group of the lowest Arabic number and a copy of Form DC-1 must be placed with the deliverables for the other Sample Delivery Group(s). The copies should be identified as "copy(ies)," and the location of the original should be noted on the copies.

Sign and date the airbill (if present). Examine the shipping container and record the presence/absence of custody seals and their condition (i.e., intact, broken) in item 1 on Form DC-1. Record the custody seal numbers in item 2.

Open the container, remove the enclosed sample documentation, and record the presence/absence of chain-of-custody record(s), SMO forms (i.e., Traffic Reports, Packing Lists), and airbills or airbill stickers in items 3-5 on Form DC-1. Specify if there is an airbill present or an airbill sticker in item 5 on Form DC-1. Record the airbill or sticker number in item 6.

Remove the samples from the shipping container(s), examine the samples and the sample tags (if present), and record the condition of the sample bottles (i.e., intact, broken, leaking) and presence or absence of sample tags in items 7 and 8 on Form DC-1.

Review the sample shipping documents and complete the header information described in Part A. Compare the information recorded on all the documents and samples and mark the appropriate answer in item 9 on Form DC-1.

If there are no problems observed during receipt, sign and date (include time) Form DC-1, the chain-of-custody record, and Traffic Report, and write the sample numbers on Form DC-1. Record the appropriate sample tags and assigned laboratory numbers if applicable. The log-in date should be recorded at the top of Form DC-1 and the date and time of cooler receipt at the laboratory should be recorded in items 10 and 11. Cross out unused columns and spaces.

If there are problems observed during receipt, contact SMO and document the contact as well as resolution of the problem on a CLP Communication Log. Following resolution, sign and date the forms as specified in the preceding paragraph and note, where appropriate, the resolution of the problem.

Record the fraction designation (if appropriate) and the specific area designation (e.g., refrigerator number) in the Sample Transfer block located in the bottom left corner of Form DC-1. Sign and date the sample transfer block.

U. Document Inventory Sheet (Form DC-2)

This form is used to record the inventory of the Complete SDG File (CSF) documents which are sent to the Region.

Organize all EPA-CSF documents as described in Exhibit B, Section II and Section III. Assemble the documents in the order specified on Form DC-2 and Sections II and III, and stamp each page with the consecutive number. (Do not number the DC-2 form). Inventory the CSF by reviewing the document numbers and recording page numbers ranges in the column provided on the Form DC-2. If there are no documents for a specific document type, enter an "NA" in the empty space.

Certain laboratory specific documents related to the CSF may not fit into a clearly defined category. The laboratory should review DC-2 to determine if it is most appropriate to place them under No. 29, 30, 31, or 32. Category 32 should be used if there is no appropriate previous category. These types of documents should be described or listed in the blanks under each appropriate category.

SECTION IV

DATA REPORTING FORMS

U.S. EPA - CLP

COVER PAGE - INORGANIC ANALYSES DATA PACKAGE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

SOW No.: _____

EPA Sample No.	Lab Sample ID.

Were ICP interelement corrections applied? Yes/No ___

Were ICP background corrections applied? Yes/No ___

If yes-were raw data generated before application of background corrections? Yes/No ___

Comments:

_____

_____

_____

_____

I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on diskette has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature.

Signature: _____ Name: _____

Date: _____ Title: _____

U.S. EPA - CLP

1

INORGANIC ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Lab Sample ID: _____

Level (low/med): _____ Date Received: _____

% Solids: _____

Concentration Units (ug/L or mg/kg dry weight): _____

CAS No.	Analyte	Concentration	C	Q	M
7429-90-5	Aluminum				
7440-36-0	Antimony				
7440-38-2	Arsenic				
7440-39-3	Barium				
7440-41-7	Beryllium				
7440-43-9	Cadmium				
7440-70-2	Calcium				
7440-47-3	Chromium				
7440-48-4	Cobalt				
7440-50-8	Copper				
7439-89-6	Iron				
7439-92-1	Lead				
7439-95-4	Magnesium				
7439-96-5	Manganese				
7439-97-6	Mercury				
7440-02-0	Nickel				
7440-09-7	Potassium				
7782-49-2	Selenium				
7440-22-4	Silver				
7440-23-5	Sodium				
7440-28-0	Thallium				
7440-62-2	Vanadium				
7440-66-6	Zinc				
	Cyanide				

Color Before: _____ Clarity Before: _____ Texture: _____

Color After: _____ Clarity After: _____ Artifacts: _____

Comments:

_____

_____

_____

_____

U.S. EPA - CLP

2A
INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Initial Calibration Source: _____

Continuing Calibration Source: _____

Concentration Units: ug/L

Analyte	Initial Calibration True	Found	%R(1)	Continuing Calibration True	Found	%R(1)	Found	%R(1)	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

(1) Control Limits: Mercury 80-120; Other Metals 90-110; Cyanide 85-115

U.S. EPA - CLP

2B
CRDL STANDARD FOR AA AND ICP

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

AA CRDL Standard Source: _____

ICP CRDL Standard Source: _____

Concentration Units: ug/L

	CRDL Standard for AA			CRDL Standard for ICP				
				Initial			Final	
Analyte	True	Found	%R	True	Found	%R	Found	%R
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								

U.S. EPA - CLP

3
BLANKS

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Preparation Blank Matrix (soil/water): _____

Preparation Blank Concentration Units (ug/L or mg/kg): _____

Analyte	Initial Calib. Blank (ug/L)	C	Continuing Calibration Blank (ug/L) 1	C	2	C	3	C	Prepa-ration Blank	C	M
Aluminum											
Antimony											
Arsenic											
Barium											
Beryllium											
Cadmium											
Calcium											
Chromium											
Cobalt											
Copper											
Iron											
Lead											
Magnesium											
Manganese											
Mercury											
Nickel											
Potassium											
Selenium											
Silver											
Sodium											
Thallium											
Vanadium											
Zinc											
Cyanide											

U.S. EPA - CLP

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ICP INTERFERENCE CHECK SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

ICP ID Number: _____ ICS Source: _____

Concentration Units: ug/L

Analyte	True Sol. A	True Sol. AB	Initial Found Sol. A	Initial Found Sol. AB	Initial Found %R	Final Found Sol. A	Final Found Sol. AB	Final Found %R
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								

U.S. EPA - CLP

5A
SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

% Solids for Sample: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit %R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Spike Added (SA)	%R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments:

U.S. EPA - CLP

5B

POST DIGEST SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

Concentration Units: ug/L

Analyte	Control Limit %R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Spike Added (SA)	%R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments:

_____

_____

_____

_____

U.S. EPA - CLP

6
DUPLICATES

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

% Solids for Sample: _____ % Solids for Duplicate: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit	Sample (S)	C	Duplicate (D)	C	RPD	Q	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								

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LABORATORY CONTROL SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Solid LCS Source: _____

Aqueous LCS Source: _____

Analyte	Aqueous (ug/L) True	Found	%R	Solid (mg/kg) True	Found	C	Limits		%R
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

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8
STANDARD ADDITION RESULTS

Lab Name: ______________________________ Contract: ____________

Lab Code: _______ Case No.: ______ SAS No.: _______ SDG No.: _______

Concentration Units: ug/L

EPA Sample No.	An	0 ADD ABS	1 ADD CON	1 ADD ABS	2 ADD CON	2 ADD ABS	3 ADD CON	3 ADD ABS	Final Conc.	r	Q

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ICP SERIAL DILUTIONS

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

Concentration Units: ug/L

Analyte	Initial Sample Result (I)	C	Serial Dilution Result (S)	C	% Difference	Q	M
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Mercury							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							

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INSTRUMENT DETECTION LIMITS (QUARTERLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

ICP ID Number: _____ Date: _____

Flame AA ID Number: _____

Furnace AA ID Number: _____

Analyte	Wave-length (nm)	Back-ground	CRDL (ug/L)	IDL (ug/L)	M
Aluminum			200		
Antimony			60		
Arsenic			10		
Barium			200		
Beryllium			5		
Cadmium			5		
Calcium			5000		
Chromium			10		
Cobalt			50		
Copper			25		
Iron			100		
Lead			3		
Magnesium			5000		
Manganese			15		
Mercury			0.2		
Nickel			40		
Potassium			5000		
Selenium			5		
Silver			10		
Sodium			5000		
Thallium			10		
Vanadium			50		
Zinc			20		

Comments:

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11A
ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

ICP ID Number: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for: Al	Ca	Fe	Mg	__
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

_____

_____

_____

_____

U.S. EPA - CLP

11B
ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

ICP ID Number: _____ Date: _____

Analyte	Wavelength (nm)	Interelement Correction Factors for:				
		___	___	___	___	___
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

_____

_____

_____

_____

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12
ICP LINEAR RANGES (QUARTERLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

ICP ID Number: _____ Date: _____

Analyte	Integ. Time (Sec.)	Concentration (ug/L)	M
Aluminum			
Antimony			
Arsenic			
Barium			
Beryllium			
Cadmium			
Calcium			
Chromium			
Cobalt			
Copper			
Iron			
Lead			
Magnesium			
Manganese			
Mercury			
Nickel			
Potassium			
Selenium			
Silver			
Sodium			
Thallium			
Vanadium			
Zinc			

Comments:

_____

_____

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_____

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PREPARATION LOG

Lab Name: ______________________________ Contract: ____________

Lab Code: ________ Case No.: ______ SAS No.: _______ SDG No.: _______

Method: __

EPA Sample No.	Preparation Date	Weight (gram)	Volume (mL)

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ANALYSIS RUN LOG

Lab Name: ____________________ Contract: ________

Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______

Instrument ID Number: ____________ Method: __

Start Date: ________ End Date: ________

EPA Sample No.	D/F	Time	% R	Analytes																							
				AL	SB	AS	BA	BE	CD	CA	CR	CO	CU	FE	PB	MG	MN	HG	NI	K	SE	AG	NA	TL	V	ZN	CN

SAMPLE LOG-IN SHEET

Lab Name	Page _ _ of _ _
Received By *(Print Name)*	Log-in Date
Received By *(Signature)*	
Case Number	Sample Delivery Group No / SAS Number

Remarks		EPA Sample #	Corresponding Sample Tag #	Corresponding Assigned Lab #	Remarks. Condition of Sample Shipment, etc
1. Custody Seal(s)	Present/Absent* Intact/Broken				
2. Custody Seal Nos.					
3. Chain-of-Custody Records	Present/Absent*				
4. Traffic Reports or Packing Lists	Present/Absent*				
5. *Airbill*	Airbill/Sticker Present/Absent*				
6. Airbill No					
7. Sample Tags	Present/Absent*				
Sample Tag Numbers	Listed/Not Listed on Chain-of-Custody				
8. Sample Condition:	Intact/Broken*/Leaking				
9. Does information on custody records, traffic reports, and sample tags agree?	Yes/No*				
10. Date Received at Lab.					
11. Time Received					
Sample Transfer					
Fraction	Fraction				
Area #	Area #				
By	By				
On	On				

* Contact SMO and attach record of resolution.

Received By	Logbook No
Date	Logbook Page No.

FULL INORGANICS
COMPLETE SDG FILE (CSF)
INVENTORY SHEET

Lab Name: _____ City/State: _____

Case No. _____ SDG No. _____ SDG Nos. to Follow: _____ _____ _____

SAS No. _____ Contract No. _____ SOW No. _____

All documents delivered in the Complete SDG File must be original documents where possible. (Reference Exhibit B, Section II D and Section III V)

		Page Nos.		(Please Check:)	
		From	To	Lab	Region
1.	Inventory Sheet (DC-2) (Do not number)			____	____
2.	Cover Page	____	____	____	____
3.	Inorganic Analysis Data Sheet (Form I-IN)	____	____	____	____
4.	Initial & Continuing Calibration Verification (Form IIA-IN)	____	____	____	____
5.	CRDL Standards For AA and ICP (Form IIB-IN)	____	____	____	____
6.	Blanks (Form III-IN)	____	____	____	____
7.	ICP Interference Check Sample (Form IV-IN)	____	____	____	____
8.	Spike Sample Recovery (Form VA-IN)	____	____	____	____
9.	Post Digest Spike Sample Recovery (Form VB-IN)	____	____	____	____
10.	Duplicates (Form VI-IN)	____	____	____	____
11.	Laboratory Control Sample (Form VII-IN)	____	____	____	____
12.	Standard Addition Results (Form VIII-IN)	____	____	____	____
13.	ICP Serial Dilutions (Form IX-IN)	____	____	____	____
14.	Instrument Detection Limits (Form X-IN)	____	____	____	____
15.	ICP Interelement Correction Factors (Form XIA-IN)	____	____	____	____
16.	ICP Interelement Correction Factors (Form XIB-IN)	____	____	____	____
17.	ICP Linear Ranges (Form XII-IN)	____	____	____	____
18.	Preparation Log (Form XIII-IN)	____	____	____	____
19.	Analysis Run Log (Form XIV-IN)	____	____	____	____
20.	ICP Raw Data	____	____	____	____
21.	Furnace AA Raw Data	____	____	____	____
22.	Mercury Raw Data	____	____	____	____

		Page Nos.		(Please Check:)	
		From	To	Lab	Region
23.	Cyanide Raw Data	___	___	___	___
24.	Preparation Logs Raw Data	___	___	___	___
25.	Percent Solids Determination Log	___	___	___	___
26.	Traffic Report	___	___	___	___
27.	EPA Shipping/Receiving Documents				
	Airbill (No. of Shipments ____)	___	___	___	___
	Chain-of-Custody Records	___	___	___	___
	Sample Tags	___	___	___	___
	Sample Log-In Sheet (Lab & DC1)	___	___	___	___
	SDG Cover Sheet	___	___	___	___
28.	Misc. Shipping/Receiving Records (list all individual records)				
	Telephone Logs	___	___	___	___
	_____	___	___	___	___
	_____	___	___	___	___
29.	Internal Lab Sample Transfer Records & Tracking Sheets (describe or list)	___	___	___	___
	_____	___	___	___	___
	_____	___	___	___	___
30.	Internal Original Sample Prep & Analysis Records (describe or list)				
	Prep Records _____	___	___	___	___
	Analysis Records _____	___	___	___	___
	Description _____	___	___	___	___
31.	Other Records (describe or list)				
	Telephone Communication Log	___	___	___	___
	_____	___	___	___	___
	_____	___	___	___	___

32. Comments:

_____

_____

Completed by (CLP Lab):

_____	_____	_____
(Signature)	(Print Name & Title)	(Date)

Audited by (EPA):

_____	_____	_____
(Signature)	(Print Name & Title)	(Date)

EXHIBIT C

INORGANIC TARGET ANALYTE LIST

INORGANIC TARGET ANALYTE LIST (TAL)

Analyte	Contract Required Detection Limit (1,2) (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	3
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20
Cyanide	10

(1) Subject to the restrictions specified in the first page of Part G, Section IV of Exhibit D (Alternate Methods - Catastrophic Failure) any analytical method specified in SOW Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the Contract Required Detection Limit. This is illustrated in the example below:

For lead:

Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 220
Contract Required Detection Limit (CRDL) = 3

The value of 220 may be reported even though the instrument detection limit is greater than CRDL. The instrument or method detection limit must be documented as described in Exhibits B and E.

(2) The CRDLs are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The detection limits for samples may be considerably higher depending on the sample matrix.

EXHIBIT D

ANALYTICAL METHODS

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SECTION I

INTRODUCTION

Inorganic Methods Flow Chart: Figure I outlines the general analytical scheme the Contractor will follow in performing analyses under this contract.

Permitted Methods: Subject to the restrictions specified in Section IV, Part G - Alternate Methods (Catastrophic ICP Failure), any analytical method specified in Exhibit D may be used as long as the documented instrument or method detection limits meet the Contract Required Detection Limits (Exhibit C). Analytical methods with higher detection limits may be used only if the sample concentration exceeds five times the documented detection limit of the instrument or method.

Initial Run Undiluted: All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range (as appropriate), re-analysis for that analyte(s) is required after appropriate dilution. The Contractor must use the least dilution necessary to bring the analyte(s) within the valid analytical range (but not below the CRDL) and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proofthat dilution was required to obtain valid results, both diluted and undiluted sample measurements must be contained in the raw data. ICP data showing a high concentration for a particular analyte, combined with an analyte result that is close to the middle range of the calibration curve in the diluted sample, constitute sufficient proof that the sample had to initially be run diluted for that analyte on a furnace AA instrument. All sample dilutions shall be made with deionized water appropriately acidified to maintain constant acid strength.

Quality Assurance/Quality Control Measurements: The Contractor is reminded and cautioned that Exhibit D is a compendium of required and/or permitted analytical methods to be used in the performance of analyses under this contract. The quality assurance/quality control procedures or measurements to be performed in association with these methods or analyses are specified in Exhibit E. In the event references to quality assurance measurements in any of the methods appear to be in conflict with or to be less stringent than the requirements of Exhibit E, the requirements of Exhibit E will prevail.

Raw Data Requirements: The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance Protocol of Exhibit E. The Raw Data Deliverables requirements are specified in Exhibit B, Section II.D.2.d. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

Glassware Cleaning: Lab glassware to be used in metals analysis must be acid cleaned according to EPA's manual "Methods for Chemical Analysis of Water and Wastes" or an equivalent procedure.

Standard Stock Solutions: Stock solutions to be used for preparing instrument or method calibration standards may be purchased or prepared as described in the individual methods of Exhibit D. All other solutions to be used for Quality Assurance/Quality Control measurements shall conform to the specific requirements of Exhibit E.

Aqueous Sample pH Measurement: Before sample preparation is initiated on an aqueous sample received in shipment, the Contractor must check the pH of the sample and note in a preparation log if the pH is <2 for a metals sample or if the pH is >12 for a cyanide sample. The Contractor shall not perform any pH adjustment action if the sample has not been properly preserved. If the sample has not been preserved, contact SMO before proceeding with the preparation and analysis for further instructions.

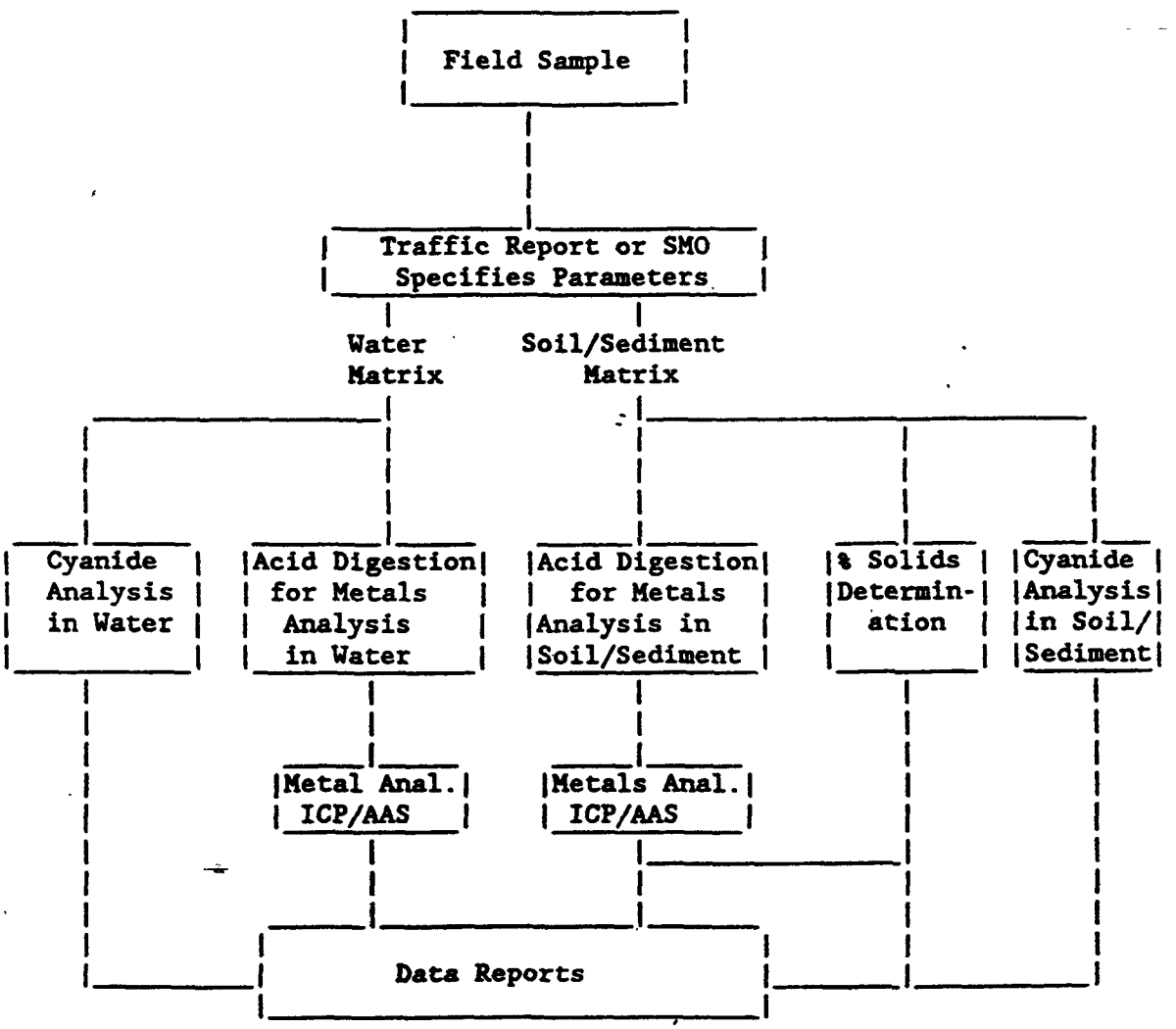
Sample Mixing: Unless instructed otherwise by the EPA Administrative Project Officer or Technical Project Officer, all samples shall be mixed thoroughly prior to aliquoting for digestion. No specific procedure is provided herein for homogenization of soil/sediment samples; however, an effort should be made to obtain a representative aliquot.

Background Corrections: Background corrections are required for Flame AA measurements below 350 nm and for all Furnace AA measurements. For ICP background correction requirements, see Exhibit D Section IV, Part A, paragraph 2.1.

Replicate Injections/Exposures: Each furnace analysis requires a minimum of two injection (burns), except for full method of standard addition (MSA). All ICP measurements shall require a minimum of two replicate exposures. Appropriate hard copy raw data for each exposure/injection shall be included in the data package in accordance with Exhibit B, Section II, Part D, paragraph 2.d. The average of each set of exposures/injections shall be used for standardization, sample analysis, and reporting as specified in Exhibit D.

Figure 1

INORGANICS METHODS FLOW CHART



SECTION II

SAMPLE PRESERVATION AND HOLDING TIMES

A. SAMPLE PRESERVATION

1. Water Sample Preservation

Measurement Parameter	Container(1)	Preservative(2)
Metals	P,G	HNO_3 to pH <2
Cyanide, total and amenable to chlorination	P,G	0.6g ascorbic acid(3) NaOH to pH >12 Cool, maintain at $4^{\circ}C(\pm 2^{\circ}C)$ until analysis

FOOTNOTES:

(1) Polyethylene (P) or glass (G).
(2) Sample preservation is performed by the sampler immediately upon sample collection.
(3) Only used in the presence of residual chlorine.

2. Soil/Sediment Sample Preservation

The preservation required for soil/sediment samples is maintenance at $4^{\circ}C$ ($\pm 2^{\circ}$) until analysis.

B. HOLDING TIMES FOR WATER AND SOIL/SEDIMENT SAMPLES

Following are the maximum sample holding times allowable under this contract. To be compliant with this contract, the Contractor must analyze samples within these times even if these times are less than the maximum data submission times allowed in this contract.

Analyte	No. of Days Following Sample Receipt by Contractor
Mercury	26 days
Metals (other than mercury)	180 days
Cyanide	12 days

SECTION III

SAMPLE PREPARATION

A. WATER SAMPLE PREPARATION

1. Acid Digestion Procedure for Furnace Atomic Absorption Analysis

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 1 mL of (1+1) HNO_3 and 2 mL 30% H_2O_2 to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

If Sb is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

2. Acid Digestion Procedure for ICP and Flame AA Analyses

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

B. SOIL/SEDIMENT SAMPLE PREPARATION

1. Acid Digestion Procedure for ICP, Flame AA and Furnace AA Analyses

a. Scope and Application

This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

b. Summary of Method

A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the Flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the Furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a percent solids determination (Section IV,Part F).

c. Apparatus and Materials

(1) 250 mL beaker or other appropriate vessel

(2) Watch glasses

(3) Thermometer that covers range of 0° to $200^{\circ}C$

(4) Whatman No. 42 filter paper or equivalent

d. Reagents

(1) ASTM Type II water (ASTM D1193): Water must be monitored.

(2) Concentrated nitric acid (sp. gr. 1.41)

(3) Concentrated hydrochloric acid (sp. gr. 1.19)

(4) Hydrogen Peroxide (30%)

e. Sample Preservation and Handling

Soil/sediment (nonaqueous) samples must be refrigerated at $4^{\circ}C$ ($\pm 2^{\circ}$) from receipt until analysis.

f. Procedure

(1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01g) a 1.0 to 1.5 g portion of sample and transfer to a beaker.

(2) Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

(3) After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

(4) Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

(5a) If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.

(5b) If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute the sample to 100 mL with Type II water (or centrifuge the sample). NOTE: In place of filtering, the sample (after dilution and

mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted digestate solution contains approximately 2% (v/v) HNO_3. Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

g. Calculations

(1) A separate determination of percent solids must be performed (Section IV, Part F).

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where,
C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample
S = % Solids/100

C. TOTAL METALS SAMPLE PREPARATION USING MICROWAVE DIGESTION

1. SCOPE AND APPLICATION

This method is an acid digestion procedure using microwave energy to prepare water and soil samples for analysis by GFAA, ICP, or Flame AA for the following metals:

Aluminum	Chromium	Potassium
Antimony*	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

*NOTE: This microwave digestion method is not appropriate for the quantitative recovery of Antimony from soil and sediment samples.

2. SUMMARY OF METHOD

a. Water Sample Preparation

A representative 45 mL water sample is digested in 5 mL of concentrated nitric acid in a Teflon^{R} PFA vessel for 20 minutes using microwave heating. The digestate is then filtered to remove insoluble material. The sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

b. Soil Sample Preparation

A representative 0.5 g (wet weight) sample is digested in 10 mL of concentrated nitric acid in a Teflon^{R} PFA vessel for 10 minutes using microwave heating. The digestate is then filtered to remove insoluble material. The sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. NOTE: This microwave digestion method is not appropriate for the quantitative recovery of Antimony from soil and sediment samples.

3. APPARATUS AND MATERIALS

a. Commercial kitchen or home-use microwave ovens shall not be used for the digestion of samples under this contract. The oven cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.

b. Microwave oven with programmable power settings up to at least 600 Watts.

c. The system must use PFA Teflon^{R} digestion vessels (120 mL capacity) capable of withstanding pressures of up to 110 ±10 psi (7.5 ±0.7 atm). These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

d. A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 rpm.

e. Polymeric volumetric ware in plastic (Teflon^{R} or polyethylene) 50 mL or 100 mL capacity.

f. Whatman No. 41 filter paper (or equivalent).

g. Disposable polypropylene filter funnel.

h. Analytical balance, 300 g capacity, and minimum ±0.01 g.

i. Polyethylene bottles, 125 mL, with caps.

4. REAGENTS

a. ASTM Type II water (ASTM D1193): water must be monitored.

b. Sub-boiled, concentrated nitric acid (sp. gr. 1.41).

c. Concentrated hydrochloric acid (sp. gr. 1.19).

5. MICROWAVE CALIBRATION PROCEDURE

a. The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every six months. The calibration data for each calibration must be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50 and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5 - 6 watts and becomes the smallest unit of power that can be controlled. If 20 - 40 watts are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 Kg of water exposed to microwave radiation for a fixed period of time. The water is placed in a Teflon® beaker (or a beaker that is made of some other material that does not adsorb microwave energy) and stirred before measuring the temperature. Glass beakers adsorb microwave energy and may not be used. The initial temperature of the water must be between 19 and 25 °C. The beaker is circulated continuously through the field for at least two (2) minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature recorded. The final reading is

the maximum temperature reading after each energy exposure. These measurements must be accurate to ± 0.1 °C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

The absorbed power is determined by the following formula:

$$P = \frac{(K)\ (Cp)\ (m)\ (DT)}{t}$$

Where:

P = The apparent power absorbed by the sample in watts (joules per second),

K = The conversion factor for thermochemical calories per second to watts (=4.184),

C_p = The heat capacity, thermal capacity, or specific heat (cal. $g^{-1}.°C^{-1}$) of water (=1.0),

m = The mass of the sample in grams (g),

DT = the final temperature minus the initial tempereture (°C), and

t = the time in seconds (s)

Using 2 minutes and 1 Kg of distilled water, the calibration equation simplifies to:

P = (DT) (34.87).

The microwave user can now relate power in watts to the percent power setting of the microwave

6. CLEANING PROCEDURE

a. <u>The initial cleaning of the PFA vessels:</u>

(1) Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.

(2) Rinse in ASTM Type I water.

(3) Immerse in 1:1 HCl for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

(4) Rinse in ASTM Type I water.

(5) Immerse in 1:1 HNO_3 for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

(6) The vessels are then rinsed with copious amounts of ASTM Type I water prior to use for any analyses under this contract.

b. Cleaning procedure between sample digestions

(1) Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.

(2) Rinse with 1:1 nitric acid.

(3) Rinse three times with ASTM Type I water. If contaminants are found in the preparation blank, it is mandatory that steps a(2) through a(6) be strictly adhered to.

7. DIGESTION PROCEDURE

a. Water Sample Digestion Procedure

(1) A 45 mL aliquot of the sample are measured into Teflon^R digestion vessels using volumetric glassware.

(2) 5 mL of high purity concentrated HNO_3 is added to the digestion vessels.

(3) The caps with the pressure release valves are placed on the vessels hand tight and then tightened, using constant torque, to 12 ft./lbs. The weight of each vessel is recorded to 0.02 g.

(4) Place 5 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave.

(5) This procedure is energy balanced for five 45 mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than 5 samples are digested, the remaining vessels must be filled with 45 mL of tap, DI or Type II water and 5 mL of concentrated nitric acid.

Newer microwave ovens may be capable of higher power settings which may allow

a larger number of samples. If the analyst wishes to digest more than 5 samples at a time, the analyst may use different power settings as long as they result in the same time temperature conditions defined in the power programming for this method.

The initial temperature of the samples should be 24 ± 1°C. The preparation blank must have 45 mL of deionized water and the same amount (5 mL) of acid that is added to the samples.

The microwave unit first-stage program must be set to give 545 watts for 10 minutes and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to 160 ±4°C in ten minutes and permits a slow rise to 165-170 °C during the second 10 minutes.

(6) Following the 20 minute program, the samples are left to cool in the microwave unit for five minutes, with the exhaust fan ON. The samples and/or carousel may then be removed from the microwave unit. Before opening the vessels, let cool until they are no longer hot to the touch.

(7) After the sample vessel has cooled, weigh the sample vessel and compare to the initial weight as reported in the preparation log. Any sample vessel exhibiting a ≤ 0.5 g loss must have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with the sample preparation. Any sample vessel exhibiting a > 0.5 g loss must be identified in the preparation log and the sample redigested.

(9) Sample Filtration:

The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. The digestates are then filtered into 50 mL glass volumetric flasks through ultra-clean filter paper and diluted to 50 mL (if necessary). The samples are now ready for analysis. The sample results must be corrected by a factor of 1.11 in order to report final concentration values based on an initial volume of 45 ml. Concentrations so determined shall be reported as "total."

b. Soil Sample Digestion Procedure

(1) Add a representative 0.5 ±0.050 grams of sample to the Teflon^{R} PFA vessel.

(2) Add 10 ±0.1 mL of concentrated nitric acid. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel.

(3) Cap the vessel, then tighten using constant torque to 12 ft/lbs, according to the manufacturer's direction.

(4) Connect the sample vessel to the overflow vessel using Teflon^{R} PFA tubing.

(5) Weigh the vessel assembly to the nearest 0.01g.

(6) Place sample vessels in groups of 2 sample vessels or 6 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. If fewer than the recommended number of samples are to be digested, i.e. 3 samples plus 1 blank then the remaining vessels must be filled with 10 mL of nitric acid to achieve the full complement of vessels.

Each sample vessel must be attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave. Connect the overflow vessel to the center well of the oven.

(7) The preparation blank must have 0.5 mL of deionized water and the same amount (10 mL) of acid that is added to the samples. The preparation blank must later be diluted to 50 mL in the same manner as the samples.

(8) Irradiate the 2 sample vessel group at 344 watts for 10 minutes, or the 6-sample vessel group at 574 watts for 10 minutes.

This program brings the samples to 175°C in 5.5 minutes, and remains between 170-180°C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most samples. The pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases, the pressure will be limited by the relief pressure of the vessel to 7.5 $\pm$0.7 atm.

(9) Allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit, with exhaust fan ON. Allow the vessels to cool to room temperature before opening. The vessels must be carefully vented and uncapped in a fume hood.

(10) Weigh each vessel assembly. If the weight of acid plus the sample has decreased by more than 10% from the original weight, discard the digests. Determine the reason for the loss. Losses typically are attributed to use of digestion time longer than ten minutes, using too large of a sample, or having improper heating conditions. Once the source of the losses has been corrected, prepare a new set of samples for digestion.

(11) Sample Filtration:

Shake the sample well to mix in any condensate within the digestion vessel before being opened. Filter the digestion vessel into a 50 mL glass volumetric flask through ultra-clean filter paper. Rinse the sample digestion vessel, cap, connecting tube, and (if venting occurred) the overflow vessel

into the 50 mL glass flask. Dilute to 50 mL. The samples are now ready for analysis. Concentrations so determined shall be reported as "total."

(12) Calculations:

The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/Kg)} = \frac{C \times V}{W \times S}$$

Where
- C = Concentration (mg/L)
- V = Final volume in liters after sample preparation
- W = Weight in kg of wet sample
- S = % Solids/100

D. MERCURY AND CYANIDE PREPARATION

Refer to each specific method in this Exhibit for mercury and cyanide preparations.

PART A - INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD[+]

Method 200.7 CLP-M*
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

1. Scope and Application

1.1 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)

1.2 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See 5.)

1.3 Table 1 lists elements along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detected limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.4 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the line are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background

[+]A bibliography citing method references appears in paragraph 11 of the method.

*CLP-M modified for the Contract Laboratory Program.

correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Safety

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

4. Interferences

4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

4.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory**, is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element.

The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L.

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The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

4.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/ or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift.

Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

4.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

4.2 Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect

must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

5. Apparatus

5.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radio frequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 Operating conditions -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

6. Reagents and Standards

6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

6.1.1 Acetic acid, conc. (sp gr 1.06).

6.1.2 Hydrochloric acid, conc. (sp gr 1.19).

6.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

6.1.4 Nitric acid, conc. (sp gr 1.41).

6.1.5 Nitric acid, (1+1): Add 500 mL conc. HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

6.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193.

6.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 hour at 105° unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

6.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolved 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

6.3.2 Antimony solution stock, 1 mL = 100 ug Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

6.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

6.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.6 Boron solution, stock, 1 mL = 100 ug B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

6.3.7 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.8 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.9 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.10 Cobalt solution stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

6.3.11 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.12 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.13 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

6.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.2043 g $(NH_4)2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

6.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with deionized, distilled water.

6.3.18 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water. Dilute to 1,000 mL.

6.3.19 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

6.3.20 Silica solution, stock, 1 mL = 100 ug SiO_2: Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.21 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

6.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.23 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.24 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.25 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.4 Mixed calibration standard solutions -- Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See NOTE in 7.4.5) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

6.4.1 Mixed standard solution I -- Manganese, beryllium, cadmium, lead, and zinc.

6.4.2 Mixed standard solution II -- Barium, copper, iron, vanadium, and cobalt.

6.4.3 Mixed standard solution III -- Molybdenum, silica, arsenic, and selenium.

6.4.4 Mixed standard solution IV -- Calcium, sodium, potassium, aluminum, chromium and nickel.

6.4.5 Mixed standard solution V -- Antimony, boron, magnesium, silver, and thallium.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

6.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (preparation blank, 3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

6.5.2 The reagent blank (or preparation blank - See Exhibit E) must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6.6 In addition the calibration standards, an instrument check standard (3.6), an interference check sample (3.7) and a quality control sample (3.8) are also required for the analyses.

6.6.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves. (See 10.1.3.)

6.6.2 The interference check sample is prepared by the analyst, or obtained from EPA if available (Exhibit E).

6.6.3 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. EPA will either supply a quality control sample or information where one of equal quality can be procured. (See 10.1.1.)

7. Procedure

7.1 Set up instrument with proper operating parameters established in Section 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

7.2 Initiate appropriate operating configuration of computer.

7.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (NOTE: For boron concentrations greater than 500 ug/L extended flush times of 1 to 2 minutes may be required.)

7.4 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See NOTE in 8.3.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 analytical samples.

7.5 A minimum of two replicate exposures are required for standardization and all QC and sample analyses. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.

8. Calculation

8.1 Reagent blanks (preparation blanks) should be treated as specified in Exhibit E.

8.2 If dilutions were performed, the appropriate factor must be applied to sample values.

8.3 Units must be clearly specified.

9. Quality Control (Instrumental)

9.1 Quality control must be performed as specified in Exhibit E.

TABLE 1 - RECOMMENDED WAVELENGTHS(2) AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength, nm(1)	Estimated Detection Limit, ug/L(2)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See(3)
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

(1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1). The use of alternate wavelengths must be reported (in nm) with the sample data.

(2) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

(3) Highly dependent on operating conditions and plasma position.

TABLE 2. EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

PART B - ATOMIC ABSORPTION METHODS, FURNACE TECHNIQUE[+]

Analyte/Method	Page No.
Antimony - Method 204.2 CLP-M*	D-29
Arsenic - Method 206.2 CLP-M	D-30
Beryllium - Method 210.2 CLP-M	D-31
Cadmium - Method 213.2 CLP-M	D-32
Chromium - Method 218.2 CLP-M	D-33
Lead - Method 239.2 CLP-M	D-34
Selenium - Method 270.2 CLP-M	D-36
Silver - Method 272.2 CLP-M	D-38
Thallium - Method 279.2 CLP-M	D-39

[+]From "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020), Metals-4, as modified for use in the Contract Laboratory Program).

*CLP-M modified for the Contract Laboratory Program.

ANTIMONY

Method 204.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 20-300 ug/L
Approximate Detection Limit: 3 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 Liter with deionized water. 1 mL = 1 mg Sb (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 800°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, contin- uous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

ARSENIC

Method 206.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 mL of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 mL conc. HNO_3 and dilute to 1 Liter. 1 mL = 1 mg As (1000 mg/1).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 mL.
3. Nickel Nitrate Solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of conc. HNO_3, 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

Sample Preparation

1. Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1100°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (ie., Al, Fe). If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.
3. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
4. If method of standard addition is required, follow the procedure given in Exhibit E).
5. The use of the Electrodeless Discharge Lamps (EDL) for the light source is recommended.

*CLP-M modified for the Contract Laboratory Program.

BERYLLIUM

Method 210.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-30 ug/L
Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586g of beryllium sulfate, $BeSO_4$, in deionized distilled water containing 2 mL concentrated nitric acid and dilute to 1 Liter. 1 mL = 1 mg Be (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, con-tinuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E)
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

CADMIUM

Method 213.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 0.5-10 ug/L
Approximate Detection Limit: 0.1 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.282g of cadmium sulfate, 3 $CdSO_4 \cdot 8\ H_2O$ (analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 Liter with deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(NH_4)2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL.
3. Prepare dilutions of stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 500°C.
3. Atomizing Time and Temp: 10 sec @ 1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Contamination from the work area is critical in cadmium analysis. Use pipette tips which are free of cadmium.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

CHROMIUM

Method 218.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under Part C methods, AA Flame Technique.
2. Calcium Nitrate solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 1 mL of 30% H_2O_2 and 1 mL of the calcium nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/L where its suppressive effect becomes constant up to 1000 mg/L.
3. Background correction is required.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipette tips have been reported to be a possible source of contamination.
6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
7. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

LEAD

Method 239.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 Liter with deionized distilled water. 1 mL = 1 mg Pb (1000mg/L).
2. Lanthanum Nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL conc. HNO_3 and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.
3. Working Lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard add 10 mL of the lanthanum nitrate solution.

Sample Preparation

1. To each 100 mL of prepared sample solution add 10 mL of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 500°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5 Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.

*CLP-M modified for the Contract Laboratory Program.

3. Greater sensitivity can be acheived using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.

4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976).

5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.

6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

7. If method of standard addition is required, follow the procedure given in Exhibit E.

SELENIUM

Method 270.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 2 ug/L

Preparation of Standard Solution

1. Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 mL. 1 mL = 1 mg Se (1000 mg/L).
2. Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2.6H_2O$ in deionized distilled water and make up to 100 mL.
3. Nickel Nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
4. Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, add 1 mL of conc. HNO_3, 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

Sample Preparation

1. Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

Instrument Parameters

1. Drying Time and Temp: 30 sec @ 125°C.
2. Charring Time and Temp: 30 sec @ 1200°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization tempera- tures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe).

*CLP-M modified for the Contract Laboratory Program.

If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.

3. Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1% nickel.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

6. The use of the Electrodeless Discharge Lamp (EDL) for the light source is recommended.

SILVER

Method 272.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-25 ug/L
Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated HNO_3 and make up to 1 Liter. 1 mL = 1 mg Ag (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. The use of halide acids should be avoided.
4. If absorption to container walls or formation of AgCl is suspected, see Part G, AA methods Flame Technique.
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

THALLIUM

Method 279.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.303g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 Liter with deionized distilled water. 1 mL = 1 mg Tl (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2400°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

PART C - ATOMIC ABSORPTION METHODS, FLAME TECHNIQUE[+]

Analyte/Method	Page No.
Calcium - Method 215.1 CLP-M*	D-41
Magnesium - Method 242.1 CLP-M	D-42
Potassium - Method 258.1 CLP-M	D-43
Sodium - Method 273.1 CLP-M	D-44

[+]From "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue", USEPA EMSL, Cincinnati, Ohio, August 1977, Revised October 1980, as modified for use in the Contract Laboratory Program.

*CLP-M modified for the Contract Laboratory Program.

CALCIUM

Method 215.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-7 mg/L using a wavelength of 422.7 nm
Sensitivity: 0.08 mg/L
Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a mimimum of dilute HCl. Dilute to 1000 mL with deionized distilled water. 1 mL = 0.5 mg Ca (500 mg/L).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 mL conc. HCl (Caution: Reaction is violent) and dilute to 500 mL with deionized distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 mL of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical inteferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975]).
4. The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

*CLP-M modified for the Contract Laboratory Program.

MAGNESIUM

Method 242.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.02-0.5 mg/L using a wavelength of 285.2 nm
Sensitivity: 0.007 mg/L
Detection Limit: 0.001 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 mL of redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 0.50 mg Mg (500 mg/L).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with deionized distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/L.
2. The following line may also be used: 202.5 nm Relative Sensitivity 25.
3. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

POTASSIUM

Method 258.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-2 mg/L using a wavelength of 766.5 nm
Sensitivity: 0.04 mg/L
Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 mL = 0.10 mg K (100 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in the buffer zone.
2. The 404.4 nm line may also be used. This line has a relative sensitivity of 500.
3. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

SODIUM

Method 273.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.03-1 mg/L using a wavelength of 589.6 nm
Sensitivity: 0.015 mg/L
Detection Limit: 0.002 mg/L

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 mL = 1 mg Na (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

*CLP-M modified for the Contract Laboratory Program.

PART D - COLD VAPOR METHODS FOR MERCURY ANALYSIS

Method	Page No.
Mercury Analysis in Water by Manual Cold Vapor Technique Method 245.1 CLP-M*	D-46
Mercury Analysis in Water by Automated Cold Vapor Technique Method 245.2 CLP-M	D-52
Mercury Analysis in Soil/Sediment by Manual Cold Vapor Technique Method 245.5 CLP-M	D-58

*CLP-M modified for the Contract Laboratory Program.

MERCURY ANALYSIS IN WATER BY MANUAL COLD VAPOR TECHNIQUE

MERCURY
Method 245.1 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system.

1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved (See 10.2).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (Exhibit D, Section II).

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

*CLP-M modified for the Contract Laboratory Program.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place.

The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

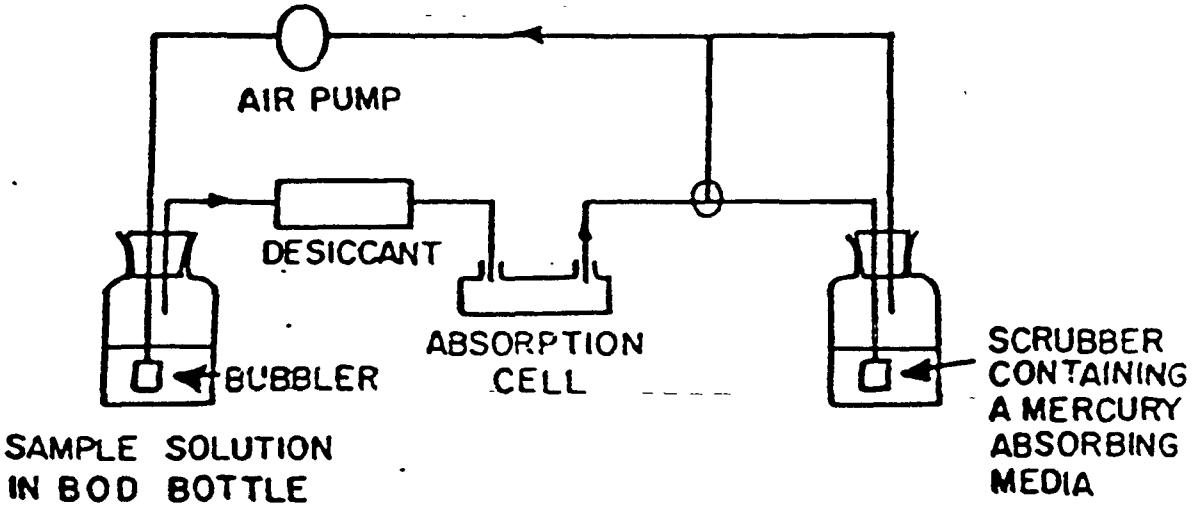
5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

Figure 1. Apparatus for Flameless Mercury Determination



6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hyroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) to each bottle. Add 15 mL of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 lbs. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation.

The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4 or
b) 0.25% iodine in a 3% a KI solution. A specially treated charcoal that will adsorb mercury vapor is available.

8. Procedure

8.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) mixing after each additon. Add 15 mL of potassium permanganate solution (6.5) to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 7). Purge the head space in the BOD bottle for at least 1 minute and add 5 mL of Stannous Sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until $KMnO_4$ is completely reduced.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/L} = \frac{\text{ug Hg in aliquot}}{\text{volume of aliquot in mL}} \times 1{,}000$$

10. Appendix

10.1 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L the standard deviations were ±0.027, ±0.0006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

10.2 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p. 349, Method D3223 (1976).

MERCURY ANALYSIS IN WATER BY AUTOMATED COLD VAPOR TECHNIQUE

MERCURY
Method 245.2 CLP-M* (Automated Cold Vapor Technique)

1. Scope and Application

1.1 The working range is 0.2 to 20.0 ug Hg/L.

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4. Interferences (see NOTE 1)

4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.

4.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.3 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All of the above interferences can be overcome by use of the Manual Mercury method.

*CLP-M modified for the Contract Laboratory Program.

5. Apparatus

5.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 mL of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1. Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of concentrated nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate (See Note 3): Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 4) Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 mL = 1.0 mg Hg.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/L.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure (See Note 5)

7.1 Set up manifold as shown in Figure 2.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as: a) equal volumes of 0.1 N $KMnO_4$(6.6) and 10% H_2SO_4 (6.1.2), or b) 0.25% iodine in a 3% KI solution, is recommended. A specially treated charcoal that will absorb mercury vapor is also available.

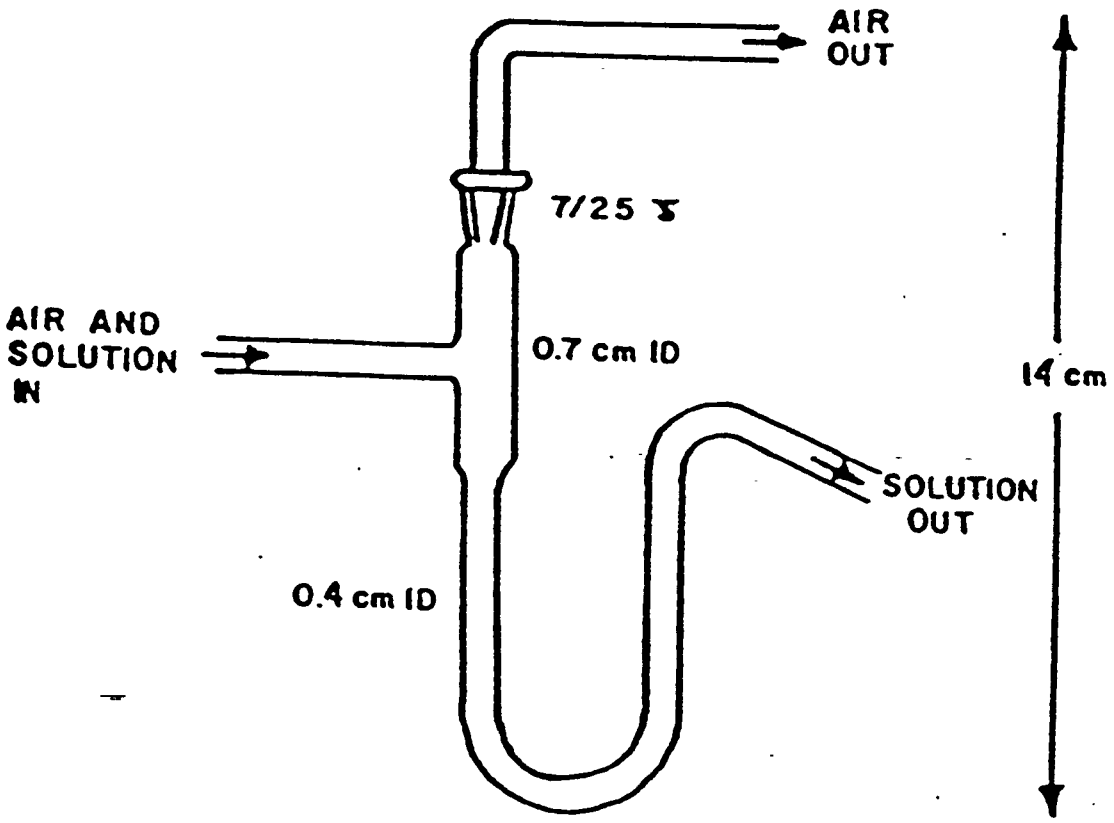


Figure 1. Vapor liquid separator

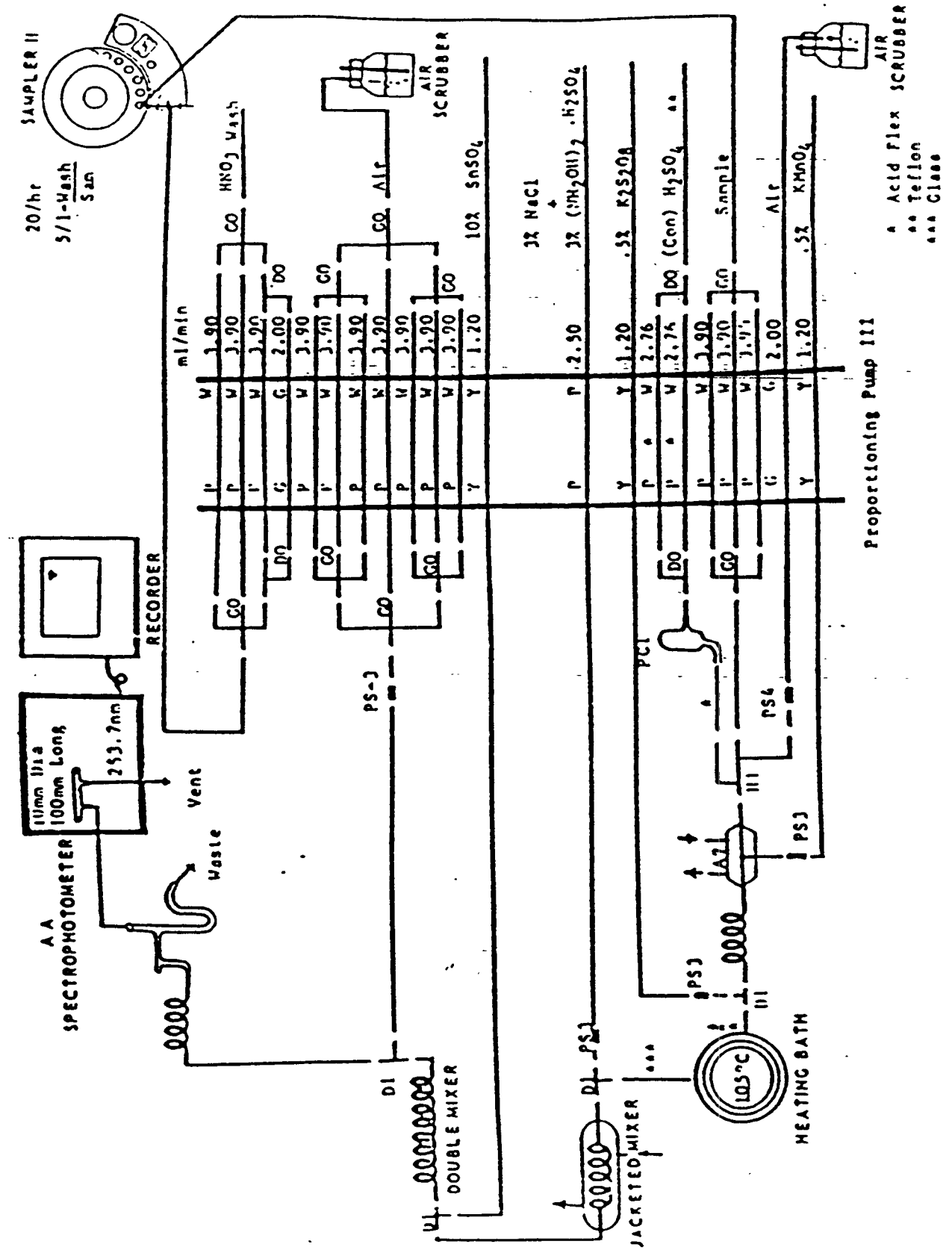


Figure 2. Mercury Manifold AA-1

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

MERCURY (in Sediments)
Method 245.5 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials

1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control

2. Summary of Method

2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique

2.2 An alternate digestion involving the use of an autoclave is described in (8.2)

3. Sample Handling and Preservation

3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.

3.2 Refrigerate solid samples at 4°C (±2°) upon receipt until analysis (see Exhibit D, Section II).

3.3 The sample should be analyzed without drying. A separate percent solids determination is required, (Part F).

4. Interferences

4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.

4.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

*CLP-M modified for the Contract Laboratory Program.

5. Apparatus

5.1 Atomic Absorption Spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells many be constructed from pexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance. Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfatory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric acid, conc.: Reagent grade of low mercury content

6.2 Nitric acid, conc.: Reagent grade of low mercury content

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use

6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 3) Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL

NOTE 3: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 = 1.0 mg Hg

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 5.0 and 10 mL aliquots of the working mercury solutions (6.8) containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of conc. H_2SO_4 (6.1) and 2.5 mL of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 mL distilled water, 15 mL of $KMnO_4$ solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury

NOTE 4: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4, or b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is also available.

8. Procedure

8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of concentrated nitric acid (6.2) mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 mL distilled water, 15 mL potassium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, purge the head space of the sample bottle for at least one minute and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1)

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 mL of conc. H_2SO_4 and 2 mL of conc. HNO_3 are added to the 0.2 g of sample. 5 mL of saturated $KMnO_4$ solution and 8 mL of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the head space of the sample bottle for at least one minute and continue as described under (7.1)

9. Calculations

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve

9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g} = \frac{\text{ug Hg in the aliquot}}{\text{wt of the aliquot in gms}}$$
(based upon dry wt of the sample)

9.3 Report mercury concentrations as described for aqueous mercury samples converted to units of mg/kg. The sample result or the detection limit for each sample must be corrected for sample weight and % solids before reporting.

PART E - METHODS FOR CYANIDE ANALYSIS

Method	Page No.
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Method for Total Cyanide Analysis in Soil/Sediment Method 335.2 CLP-M	D-71
Method for Total Cyanide Analysis by Midi Distillation Method 335.2 CLP-M	D-82

*CLP-M Modified for the Contract Laboratory Program.

METHOD FOR TOTAL CYANIDE ANALYSIS IN WATER

CYANIDE, TOTAL (in Water)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylaminobenzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.25 mg/250 mL of absorbing liquid). (Option A, 8.2).

1.3 The manual colorometric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.01 mg/L. (Option B, 8.3).

1.4 The working range of the semi-automated spectrophotometric method is 0.020 to 0.200 mg/L. Higher level samples must be diluted to fall within the working range. (Option C, 8.4).

2. Summary of Method

2.1 The cyanide as (HRN) hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridinebarbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers.

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*CLP-M Modified for the Contract Laboratory Program.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

4.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH> 12) at the time of collection (Exhibit D, Section II).

4.4 Samples must be stored at $4^{\circ}C(\pm 2^{\circ}C)$ and must be analyzed within the holding time specified in Exhibit D, Section II.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.

5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in 4.3.

5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 mL (for titration)

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).

6.4 Technicon AA II System or equivalent instrumentation, (for automated spectrophotometric method) including:

6.4.1 Sampler

6.4.2 Pump III

6.4.3 Cyanide Manifold (Figure 3)

6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters

6.4.5 Recorder

6.4.6 Data System (optional)

6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.1.2 Cadmium carbonate: powdered

7.1.3 Ascorbic acid: crystals

7.1.4 Sulfuric acid: concentrated

7.1.5 Magnesium chloride solution: Weight 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 mL flask, dissolved and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.

7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water.

7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).

7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weight out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone.

7.2.6 Sodium hydroxide solution, 0.25 N: Dissolve 10 g or NaOH in distilled water and dilute to 1 liter.

7.3 Manual Spectrophotometric Reagents

7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in a liter of distilled water. Refrigerate this solution.

7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.3.3 Color Reagent-One of the following may be used:

7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.3.2 Pyridine-pyrazolone solution:7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.1 3-Methyl-1phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.2 3,3'Dimethyl-1,1'-diphenyl [4,4'-bi-2 pyrazolin]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.

7.4.2 Phosphate buffer: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C(±2°C).

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of

concentrated HCl and mix. Dilute to about 900 mL with distilled water and mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C(±2°C).

7.4.4 Sampler wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Place 500 mL of sample in the 1 liter boiling flask. Add 50 mL, of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.3 Slowly add 25 mL concentrated sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.2 Titrimetric Determination (Option A)

8.2.1 If the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 mL of sodium phosphate solution (7.3.1) and mix. The dilution factor must be reported on Form XIV.

8.3.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell. NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Detection Limit (CRDL). To each standard, add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

mL of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 mL
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	75
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not

agree within ±15% of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding.

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL).

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

mL Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/L
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C)

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

9.1 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/L} = \frac{(A-B)\ 1{,}000\ \text{mL/L}}{\text{mL orig. sample}} \times \frac{250\ \text{mL}}{\text{mL of aliquot titrated}}$$

WHERE: A = volume of $AgNO_3$ for titration of sample (1 mL = 1 mg Ag)

B = volume of $AgNO_3$ for titration of blank (1 mL = 1 mg Ag)

AND: 250 mL = distillate volume (See 8.1.5)
1000 mL = conversion mL to L
mL original sample (See 8.1.1)
mL of aliquot titrated (See 8.2.1)

9.2 If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 mL and the distillate volume was 250 mL). Also, correct for, and report on Form XIV, any dilutions which were made before or after distillation.

The minimum concentration that can be reported from the calibration curve is 20 ug/L that corresponds to 10 ug/L in a sample that has been distilled.

9.3 If the colorimetric procedure is used, calculate the cyanide, in ug/L, in the original sample as follows:

$$\text{CN, ug/L} = \frac{A \times 1{,}000 \text{ mL/L}}{B} \times \frac{50 \text{ mL}}{C}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = mL of original sample for distillation (See 8.1.1)
C = mL taken for colorimetric analysis (See 8.3.1)

AND: 50 mL = volume of original sample aliquot (See 8.3.1)
1000 mL/L = conversion mL to L

The minimum value that can be substituted for A is 5 ug per 250 mL. That yields a concentration of 10 ug/L in the distilled sample.

METHOD FOR TOTAL CYANIDE ANALYSIS IN SOIL/SEDIMENT

CYANIDE, TOTAL (in Sediments)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in sediments and other solids.

1.2 The detection limit is dependent upon the weight of sample taken for analysis.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone for 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 Samples must be stored at $4^{\circ}C(\pm 2^{\circ}C)$ and must be analyzed within the holding time specified in Exhibit D, Section II.

4.2 Samples are not dried prior to analysis. A separate percent solids determination must be made in accordance with the procedure in Part F.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.

5.2 Sulfides adversely affect the colorimetric and titration procedures.

*CLP-M Modified for the Contract Laboratory Program.

5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as DOW Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 mL (for titration)

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 Technicon AA II System or equivalent instrumentation (for automated spectrophotometric method) including:

6.4.1 Sampler

6.4.2 Pump III

6.4.3 Cyanide Manifold (Figure 3)

6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters

6.4.5 Recorder

6.4.6 Data System (optional)

6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.1.2 Cadmium carbonate: powdered

7.1.3 Ascorbic acid: crystals

7.1.4 Sulfuric acid: concentrated

7.1.5 Magnesium chloride solution: Weigh 510 g of $MgCl2.6H_2O$ into a 1000 mL flask, dissolve and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.

7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water (1 mL = 50.0 ug).

7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).

7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 mL acetone.

7.3 Manual Spectrophotometric Reagents

7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.3.3 Color reagent - One of the following may be used:

7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.3.2 Pyridine-pyrazolone solution:

7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.2 3,3'Dimethyl-1,1'-diphenyl-[4,4'-bi-2-pyrazolin]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this

does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.

7.4.2 Phosphate Buffer: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C.

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of conc. HCl mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.

7.4.4 Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Accurately weigh a representative 1-5 g portion of wet sample and transfer it to a boiling flask. Add 500 mL of distilled water. Shake or stir the sample so that it is dispersed.

8.1.2 Add 50 mL of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

8.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.4 Slowly add 25 mL of conc. sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.2 Titrimetric Determination (Option A)

8.2.1 If the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 mL of sodium phosphate solution (7.3.2) and mix.

8.3.1.1 Pyridine-barbituric acid method: Add 2 mL of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks.

NOTE: One calibration standard, must be made at the CRDL. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. Standards must bracket the concentrations of the sample. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

mL of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 mL
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	75
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If the distilled standard does not agree within +15% of the undistilled standards the operator should find and correct the cause of the apparent error before proceeding.

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL)

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

mL Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/L
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C).

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record

the STD CAL value. Reestablish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

9.1 A separate determination of percent solids must be performed (see Part F).

9.2 The concentration of cyanide in the sample is determined as follows.

9.2.1 (Titration)

$$\text{CN, mg/kg} = \frac{(A - B) \times \frac{250\ \text{mL}}{\text{mL aliquot titrated}} \times 1000\ \text{g/kg}}{C \times \frac{\%\text{solids}}{100}}$$

WHERE: A = mL of $AgNO_3$ for titration of sample (1 mL = 1 mg Ag)
B = mL of $AgNO_3$ for titration of blank (1 mL = 1 mg Ag)
C = wet weight of original sample in g (See 8.1.1)

AND: 250 mL = volume of distillate (See 8.1.6)
1000 g/kg = conversion factor g to kg
mL aliquot titrated (See 8.2.1)
% solids (see Part F)

9.2.2 (Manual Spectrophotometric)

$$\text{CN, mg/kg} = \frac{A \times \frac{50\ \text{mL}}{B}}{C \times \frac{\%\ \text{solids}}{100}}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = mL of distillate taken for colorimetric determination (8.3.1)
C = wet weight of original sample in g (See 8.1.1)

The minimum value that can be substituted for A is 5 ug/250 mL. That yields a concentration of 10 ug/L in the distilled sample.

AND: 50 mL = volume of standard taken for colorimetric determination (See 8.3.1)
% solids (see Part F)

9.2.3 (Semi-Automated Spectrophotometric)

If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates.

$$\text{CN, mg/kg} = \frac{A \times .25}{C \times \frac{\% \text{ solids}}{100}}$$

WHERE: A = ug/L determined from standard curve
C = wet weight of original sample in g (See 8.1.1)

AND: .25 = conversion factor for distillate final volume (See 8.1.6)
% solids (see Part F)

The minimum value that can be substituted for A is 5 ug/250 mL.

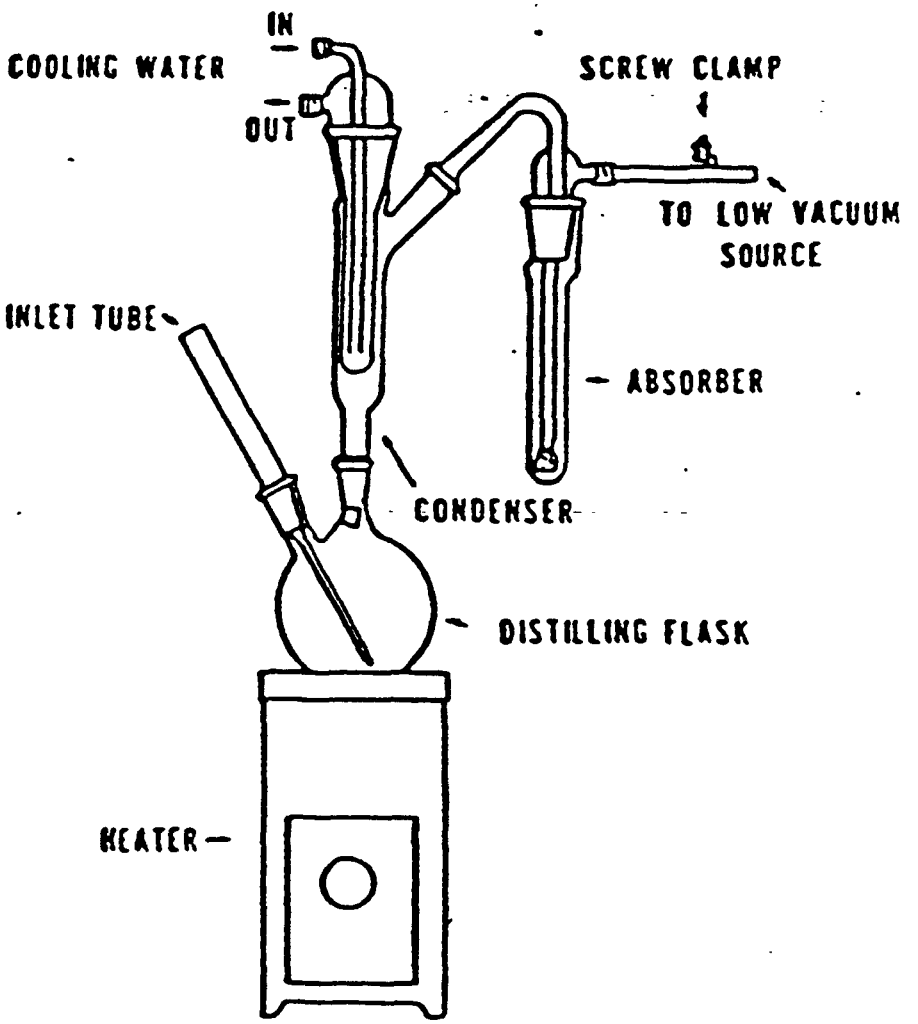

Figure 1. Cyanide distillation apparatus

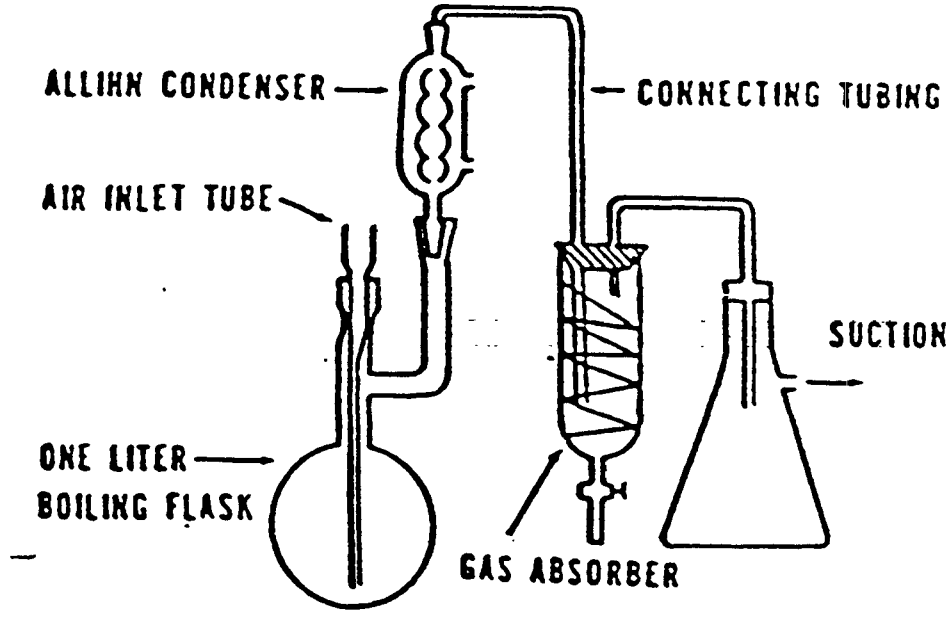

Figure 2. Cyanide distillation apparatus

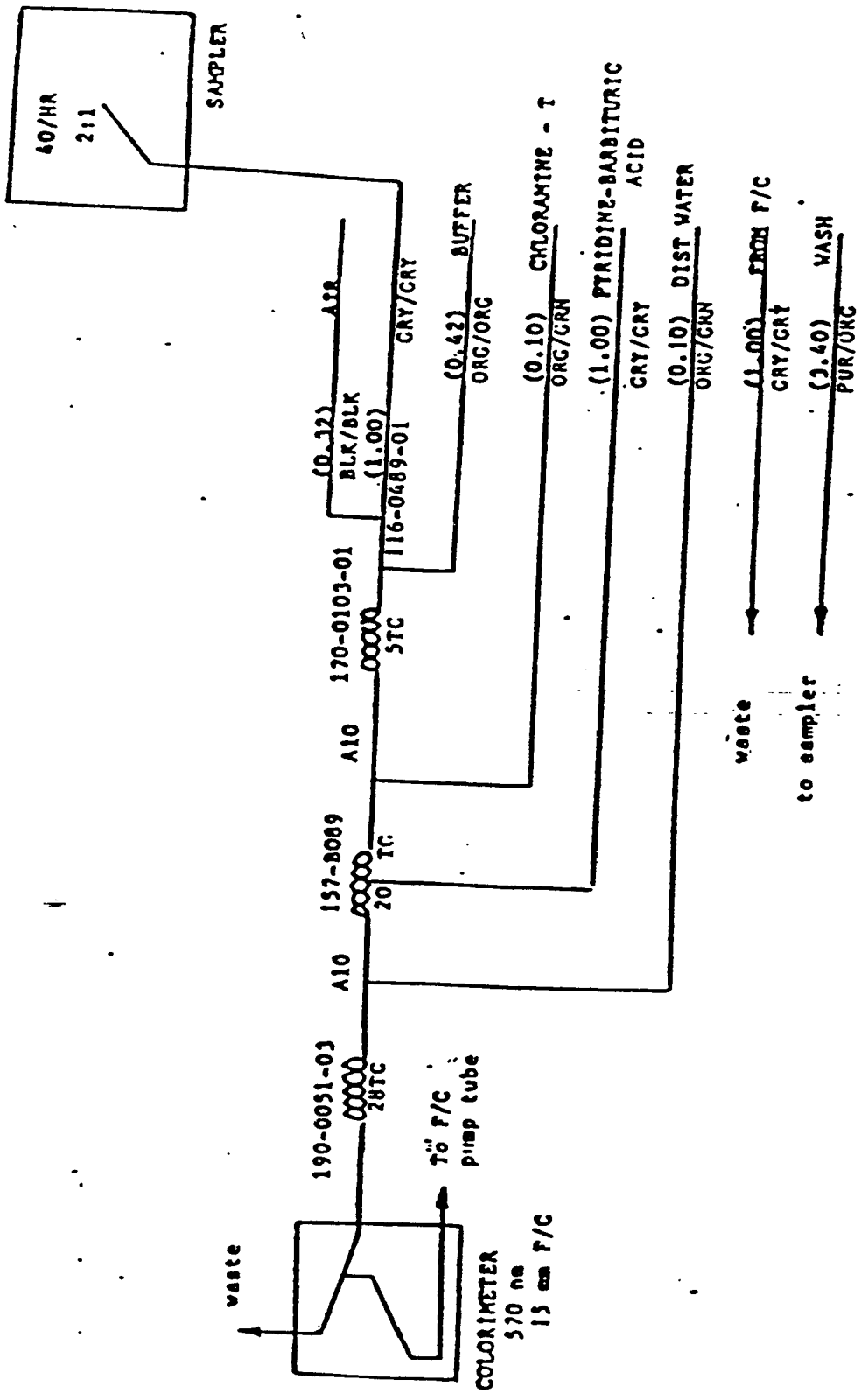

Figure 3. Cyanide Manifold

METHOD FOR TOTAL CYANIDE ANALYSIS BY MIDI DISTILLATION

CYANIDE, TOTAL (water and soils)

Method 335.2 CLP-M (Semi-automated Spectrophotometric)

1. Scope and Application

1.1 Cyanide determined by this method is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system with mineral acid in the presence of magnesium ion.

1.2 This method covers the determination of cyanide by midi distillation with a semi-automated colorimetric analysis of the distillate.

1.3 The detection limit for the semi-automated colorimetric method is approximately 10 ug/L.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a midi reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8 without hydrolysis to the cyanate. After the reaction is complete, color is formed on the addition of pyridinebarbituric acid reagent. The absorbance is read at 580 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the samples and the standards.

3. Sample Handling and Preservation

3.1 All bottles must be thoughly cleansed and rinsed to remove soluble materials from containers.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-Starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add additional 0.6 g of ascorbic acid for each liter of sample volume.

3.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH > 12) at the time of collection.

3.4 Samples must be stored at 4°C (±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

4. Interferences

4.1 Interferences are eliminated or reduced by using the distillation procedure.

4.2 Sulfides adversely affect the colorimetric procedures. If a drop of distillate on lead acetate test paper indicates the presence of sulfides, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker. and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

4.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoaming agent will prevent the foam from collecting in the condenser.

5. Apparatus

5.1 Midi reflux distillation apparatus as shown in figure 1.

5.2 Heating block - Capable of maintaining 125°C ±5°C.

5.3 Auto analyzer system with accessories:

5.3.1 Sampler

5.3.2 Pump

5.3.3 Cyanide cartridge

5.3.4 Colorimeter with 50 mm flowcells and 580 nm filter

5.3.5 Chart recorder or data system.

5.4 Assorted volumetric glassware, pipets, and micropipets.

6. Reagents

6.1 Distillation and Preparation Reagents

6.1.1 Sodium hydroxide absorbing solution, and sample wash solution, 0.25 N. Dissolve 10.0 g NaOH in ASTM Type II water and dilute to one liter.

6.1.2 Magnesium chloride solution, 51% (w/v). Dissolve 510 g of $MgCl_2$-$6H_2O$ in ASTM Type II water and dilute to one liter.

6.1.3 Sulfuric acid, 50% (v/v). Carefully add a portion of concentrated H_2SO_4 to an equal portion of ASTM Type II water.

6.1.4 Sodium hydroxide solution, 1.25 N. Dissolve 50 g of NaOH in ASTM Type II water and dilute to one liter.

6.2 Standards

6.2.1 Stock cyanide solution, 1000 mg/L CN. Dissolve 2.51 g of KCN and 2.0 g KOH in ASTM Type II water and dilute one liter. Standardize with 0.0192 N $AgNO_3$.

6.2.2 Intermediate cyanide standard solution, 10 mg/L CN. Dilute 1.0 mL of stock cyanide solution (6.2.1) plus 20 mL of 1.25 N NaOH solution (6.1.4) to 100 mL with ASTM Type II water. Prepare this solution at time of analysis.

6.2.3 Rhodamine indicator. Dissolve 20 mg of p-dimethylamino-benzal-rhodamine in 100 mL acetone.

6.2.4 Silver nitrate solution, 0.0192 N. Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to a constant weight at 104°C. Weigh out 3.2647 g of dried $AgNO_3$ and dissolve in ASTM Type II water. Dilute to one liter (1 mL corresponds to 1 mg CN).

6.2.5 Potassium chromate indicator solution. Dissolve 50 g K_2CRO_4 in sufficient ASTM Type II water. Add silver nitrate solution until a definite red precipitate is formed. Let stand for at least 12 hours, filter, and dilute to one liter with ASTM Type II water.

6.2.6 Primary standard sodium chloride, 0.0141 N. Dissolve 824.1 mg NaCl (NBS-dried 20 minutes at 104°C) in ASTM Type II water and dilute to one liter.

6.2.7 Sodium hydroxide solution, 0.1 N. Dissolve 4 g of NaOH in ASTM Type II water and dilute to one liter.

6.3 Semi-Automated Spectrophotometric Reagents

6.3.1 Phosphate buffer solution, 1 M. Dissolve 138 g of NaH_2PO_4-H_2O in ASTM Type II water and dilute to one liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C.

6.3.2 Chloramine-T solution, 0.4% (w/v). Dissolve 0.4 g of chloramine-T in ASTM Type II water and dilute to 100 mL. Prepare fresh at time of analysis.

6.3.3 Color Reagent Solution, Pyridine barbituric acid color reagent solution. Prepare this solution in the hood. Transfer 15 g of barbituric acid into a one liter Erlenmeyer flask. Add about 100 mL of ASTM Type II water and swirl the flask to mix. Add 75 mL of pyridine and 15 mL concentrated HCL and mix until all the barbituric acid is dissolved. Dilute to one liter with ASTM Type II water and store at 4°C.

7. Procedure

7.1 Distillation

7.1.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 50 mLs or less for aqueous samples and one gram for solid materials. NOTE: All samples must initally be run undiluted (i.e., aqueous samples must first be run with a 50 mL aliquot and solid samples using a one gram sample). When the cyanide concentration exceeds the highest calibration standard, appropriate dilution (but not below the CRDL) and reanalysis of the sample is required. The dilution factor must be reported on Form XIV.

7.1.2 For aqueous samples: Pipet 50 mL of sample, or an aliquot diluted to 50 mL, into the distillation flask along with 2 or 3 boiling chips.

7.1.3 For solid samples: Weigh 1.0 g of sample (to the nearest 0.01 g) into the distillation flask and dilute to 50 mL with ASTM Type II water. Add 2 or 3 boiling chips.

7.1.4 Add 50 mL of 0.25 N NaOH (6.1.1) to the gas absorbing impinger.

7.1.5 Connect the boiling flask, condenser, and absorber in the train as shown in figure 2. The excess cyanide trap contains 0.5 N NaOH.

7.1.6 Turn on the vacuum and adjust the gang (Whitney) values to give a flow of three bubbles per second from the impingers in each reaction vessel.

7.1.7 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (6.1.3) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes. (NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.)

7.1.8 Add 2 mL of magnesium chloride solution (6.1.2) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of another 2 mL of magnesium chloride solution.

7.1.9 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

7.1.10 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

7.1.11 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section II.

7.2 Semi-Automated Spectrophotometric Determination

7.2.1 Operating conditions: Because of the difference between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. The analyst should follow the instructions provided by the manufacturer of the particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

The following general procedure applies to most semi-automated colorimeters. Set up the manifold and complete system per manufacturer's instructions. Allow the colorimeter and recorder warm up for at least 30 minutes prior to use. Establish a steady reagent baseline feeding ASTM Type II water through the sample line and appropriate reagents (6.3) through reagent lines. Adjust the baseline using the appropriate control on the colorimeter.

7.2.2 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of standard solution into 50 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Detection Limit (CRDL).

As an example, standard solutions could be prepared as follows:

Total ug CN standard solution	mL 10 mg/L CN	mL 0.05 N NaOH
0.00	0.000	20
0.10	0.010	20
0.25	0.025	20
0.50	0.050	20
1.00	0.100	20
2.00	0.200	20
5.00	0.500	20

7.2.2.1 Dilute standards to 50 mL using ASTM Type II water. It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve for each SDG to ensure the distillation technique is reliable. If the distilled standard does not agree within ±15% of the undistilled standards, the operator must find and correct the cause of the error before proceeding.

7.2.3 Aspirate the highest calibration standard and adjust the colorimeter until the desired (maximum) signal-range is obtained.

7.2.4 Place calibration standards, blanks, control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

7.2.5 Switch sample line from the ASTM Type II water to sampler, set the appropriate sampling rate and begin the analysis.

8. Calculations

8.1 Calculations for Semi-automated Colorimetric Determination

8.1.1 Prepare a standard curve by plotting absorbance (peak heights, determined visually or using a data system) of standards (y) versus cyanide concentration values (total ug CN/L) (x). Perform a linear regression analysis.

8.1.2 Multiply all distilled values by the standardization value to correct for the stock cyanide solution not being exactly 1000 mg/L (See 6.2.1).

8.1.3 Using the regression analysis equation, calculate sample receiving solution concentrations from the calibration curve.

8.1.4 Calculate the cyanide of aqueous samples in ug/L of original sample, as follows:

$$\text{CN, ug/L} = \frac{A \times D \times F}{B}$$

where:
A = ug/L CN of sample from regression analysis
B = Liter of original sample for distillation (0.050 L) (See 7.1.2)
D = any dilution factor necessary to bracket sample value within standard values
F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is 10 ug/L.

8.1.5 Calculate the cyanide of solid samples in mg/kg of original sample, as follows:

8.1.5.1 A separate determination of percent solids must be performed (See Part F).

8.1.5.2 The concentration of cyanide in the sample is determined as follows:

$$\text{CN, mg/kg} = \frac{A \times D \times F}{B \times E}$$

where:
A = ug/L CN of sample from regression analysis curve
B = wet weight of original sample in g (See 7.1.3)

D = any dilution factor necessary to bracket sample value within standard values

E = % solids (See Part F)/100.

F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is 10 ug/L

PART F - PERCENT SOLIDS DETERMINATION PROCEDURE

1. Immediately following the weighing of the sample to be processed for analysis (see Section III, Part B- Soil/Sediment Sample Preparation), add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.

2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.

3. Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.* Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.

4. Duplicate percent solids determinations are required at the same frequency as are other analytical determinations. Duplicate results are to be recorded on FORM VI-IN.

5. For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.

6. Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate FORM I-IN and, where applicable, FORM VI-IN . This value will be used for calculating analytical concentration on a dry weight basis.

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

*For the purpose of paragraph 3, drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

PART G - ALTERNATE METHODS (CATASTROPHIC ICP FAILURE)+

Analyte	Page No.
Aluminum - Method 202.2 CLP-M*, Furnace AA	D-92
Barium - Method 208.2 CLP-M, Furnace AA	D-93
Cobalt - Method 219.2 CLP-M, Furnace AA	D-94
Copper - Method 220.2 CLP-M, Furnace AA	D-95
Iron - Method 236.2 CLP-M, Furnace AA	D-96
Manganese - Method 243.2 CLP-M, Furnace AA	D-97
Nickel - Method 249.2 CLP-M, Furnace AA	D-98
Vanadium - Method 286.2 CLP-M, Furnace AA	D-99
Zinc - Method 289.2 CLP-M, Furnace AA	D-100
Aluminum - Method 202.1 CLP-M, Flame AA	D-102
Antimony - Method 204.1 CLP-M, Flame AA	D-104
Barium - Method 208.1 CLP-M, Flame AA	D-105
Beryllium - Method 210.1 CLP-M, Flame AA	D-106
Cadmium - Method 213.1 CLP-M, Flame AA	D-107
Chromium - Method 218.1 CLP-M, Flame AA	D-108
Cobalt - Method 219.1 CLP-M, Flame AA	D-109
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Iron - Method 236.1 CLP-M, Flame AA	D-111
Lead - Method 239.1 CLP-M, Flame AA	D-112
Manganese - Method 243.1 CLP-M, Flame AA	D-113
Nickel - Method 249.1 CLP-M, Flame AA	D-114
Silver - Method 272.1 CLP-M, Flame AA	D-115
Thallium - Method 279.1 CLP-M, Flame AA	D-117
Vanadium - Method 286.1 CLP-M, Flame AA	D-118
Zinc - Method 289.1 CLP-M, Flame AA	D-119

+Furnace AA Methods are from "Methods for Chemical Analysis of Water and Wastes", (EPA-600/4-79-02), March 1979, as modified for use in the Contract Laboratory Program (CLP). Flame AA (Flame Technique) Methods are from "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980, as modified for use in the CLP.

*CLP-M Modified for the Contract Laboratory Program.

CONDITIONS FOR USE OF ALTERNATE METHODS

The methods contained in Part G may be used only if all of the following conditions are met:

1) Catastrophic failure of ICP occurs,

2) Administrative Project Officer authorization for use of alternate methods is granted, and

3) The IDLs for the instrumentation have been determined, as per Exhibit E, within the current calendar quarter.

ALUMINUM*

Method 202.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 20-200 ug/L
Approximate Detection Limit: 3 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 202.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1300°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 309.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only.

2. Background correction is required.

3. It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore the use of halide acids and nitrogen as a purge gas should be avoided.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

BARIUM*

Method 208.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 10-200 ug/L
Approximate Detection Limit: 2 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 208.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°.
2. Ashing Time and Temp: 30 sec @ 1200°C.
3. Atomizing Time and Temp: 10 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 553.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and pyrolytic graphite and are to be used as guidelines only.

2. The use of halide acid should be avoided.

3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COBALT*

Method 219.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 219.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 900°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 240.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization c furnace using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is required.

3. Nitrogen may also be used as the purge gas but with reported low sensitivity.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COPPER*

Method 220.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 220.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 900°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 324.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. Background correction is required.

3. Nitrogen may also be used as the purge gas.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

IRON*

Method 236.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 236.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 248.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is required.

3. Nitrogen may also be used as the purge gas.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

MANGANESE*

Method 243.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-30 ug/L
Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 243.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 279.5 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is required.

3. Nitrogen may also be used as the purge gas.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

NICKEL*

Method 249.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 249.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 900°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is required.

3. Nitrogen may also be used as the purge gas.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

VANADIUM*

Method 286.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 10-200 ug/L
Approximate Detection Limit: 4 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 286.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1400°C.
3. Atomizing Time and Temp: 15 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 318.4 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is required.

3. Because of possible chemical interaction, nitrogen should not be used as the purge gas.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

ZINC*

Method 289.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 0.2-4 ug/L
Approximate Detection Limit: 0.05 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 289.1 CLP-M).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2500°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 213.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods then the above recommended settings.

2. The use of background correction is required.

3. Nitrogen may also be used as the purge gas.

4. The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipette tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

6. If method of standard addition is required, follow the procedure given in Exhibit E.

ALUMINUM*

Method 202.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 5-50 mg/L using a wavelength of 309.3 nm
Sensitivity: 1 mg/L
Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1,000 g of aluminum metal analytical reagent grade). Add 15 mL of conc. HCl and 5 mL conc. HNO_3 to the metal, cover the beaker and warm gently. When solution is complete, transfer quantitatively to a liter volumetric flask and make up to volume with deionized distilled water. 1 mL = 1 mg Al (1000 mg/L).

2. Potassium Chloride Solution: Dissolve 95 g potassium chloride (KCl) in deionized distilled water and make up to 1 liter.

3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride solution.

Instrument Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 309.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem may be controlled by the addition of an alkali metal (potassium, 1000 ug/mL) to both sample and standard solutions.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

Notes

1. The following may also be used:

   308.2 nm Relative Sensitivity 1
   396.2 nm Relative Sensitivity 2
   394.4 nm Relative Sensitivity 2.5

2. For concentrations of aluminum below 0.3 mg/L, use of Furnace Technique (Method 202.2 CLP-M) is recommended.

ANTIMONY*

Method 204.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-40 mg/L using a wavelength of 217.6 nm
Sensitivity: 0.5 mg/L
Approximate Detection Limit: 0.2 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Sb (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Interferences

1. In the presence of lead (1000 mg/L), a special interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.

2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards must be matched.

Notes

1. For concentrations of antimony below 0.35 mg/L, use of the Furnace Technique (Method 204.2 CLP-M) is recommended.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

BARIUM*

Method 208.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-20 mg/L using a wavelength of 553.6 nm
Sensitivity: 0.4 mg/L
Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g of barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to liter. 1 mL = 1 mg Ba (1000 mg/L).

2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.

3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/L) to standards and samples alike to control this effect.

2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/L lanthanum.

Notes

1. For concentrations of barium below 0.2 mg/L, use of the Furnace Technique (Method 208.2 CLP-M) is recommended.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

BERYLLIUM*

Method 210.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.052 mg/L using a wavelength of 234.9 nm
Sensitivity: 0.025 mg/L
Approximate Detection Limit: 0.005 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 11.6586 g of beryllium sulfate, $BeSO_4$, in deionized distilled water containing 2 mL conc. nitric acid and dilute to 1 liter. 1 mL = 1 mg Be (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Sodium and silicon at concentrations in excess of 1000 mg/L have been found to severely depress the beryllium absorbance.

2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.

3. Aluminum at concentrations of 500 ug/L is reported to depress the sensitivity of beryllium [Spectrochim Acta 22, 1325 (1966)].

Notes

1. For concentrations of beryllium below 0.02 mg/L, use of the Furnace Technique (Method 210.2 CLP-M) is recommended.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

CADMIUM*

Method 213.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.052 mg/L using a wavelength of 228.8 nm
Sensitivity: 0.025 mg/L
Approximate Detection Limit: 0.005 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with dionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of cadmium below 20 ug/L, use of the Furnace Technique, Method 213.2 CLP-M is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

CHROMIUM*

Method 218.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.5-10 mg/L using a wavelength of 357.9 nm
Sensitivity: 0.25 mg/L
Approximate Detection Limit: 0.05 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Cr (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Notes

1. The following wavelengths may also be used:

   359.3 nm Relative Sensitivity 1.4
   425.4 nm Relative Sensitivity 2
   427.5 nm Relative Sensitivity 3
   428.9 nm Relative Sensitivity 4

2. The fuel rich air-acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.
3. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta 20, 631 (1973)]. A 1% oxine solution is also reported to be useful.
4. For concentrations of chromium between 50 and 200 ug/L where the air-acetylene flame cannot be used or for concentrations below 50 ug/L, use of the Furnace Technique (Method 218.2 CLP-M) is recommended.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COBALT*

Method 219.1** CLP-M (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.5-5 mg/L using a wavelength of 240.7 nm
Sensitivity: 0.2 mg/L
Approximate Detection Limit: 0.05 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.307 g of cobaltous chloride (CoCl2. 6H2O analytical reagent grade), in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Co (1000 mg/L).

2. Prepare dilutions of the stock cobalt solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Cobalt hollow cathode lamp
2. Wavelength: 240.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of cobalt below 100 ug/L use of the Furnace Technique (Method 219.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COPPER*

Method 220.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-5 mg/L using a wavelength of 324.7 nm
Sensitivity: 0.1 mg/L
Approximate Detection Limit: 0.02 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 100 g of electrolyte copper (analytical reagent grade). Dissolve in 5 mL redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per mL (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of copper below 50 ug/L use of the Furnace Technique (Method 220.2 CLP-M) is recommended.

2. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentrations. The following lines may be used:

   327.4 nm Relative Sensitivity 2
   216.5 nm Relative Sensitivity 7
   222.5 nm Relative Sensitivity 20

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

IRON*

Method 236.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.3-5 mg/L using a wavelength of 248.3 nm
Sensitivity: 0.12 mg/L
Approximate Detection Limit: 0.03 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 mL redistilled HNO_3, warming if necessary. When solution is complete, make up to 1 liter with deionized distilled water. 1 mL = 1 mg Fe (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 248.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The following wavelengths may also be used:

   248.8 nm Relative Sensitivity 2
   271.9 nm Relative Sensitivity 4
   302.1 nm Relative Sensitivity 5
   252.7 nm Relative Sensitivity 6
   372.0 nm Relative Sensitivity 10

2. For concentrations of iron below 0.05 mg/L use of the Furnace Technique (Method 236.2 CLP-M) is recommended.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

LEAD*

Method 239.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-20 mg/L using a wavelength of 283.3 nm
Sensitivity: 0.5 mg/L
Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve deionized distilled water. When solution is complete acidify with 10 mL redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Pb (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.

2. The concentrations of lead below 200 ug/L use of the Furnace Technique (Method 239.2 CLP-M) is recommended.

3. The following wavelengths may also be used:

   217.0 nm Relative Sensitivity 0.4
   261.4 nm Relative Sensitivity 10

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

MANGANESE*

Method 243.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-3 mg/L using a wavelength of 279.5 nm
Sensitivity: 0.05 mg/L
Approximate Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of manganese metal (analytical reagent grade), and dissolve in 10 mL redistilled HNO_3. When solution is complete, dilute to 1 liter with 1% (v/v) HCl. 1 mL = 1 mg Mn (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 279.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of manganese below 25 ug/L, use of the Furnace Technique (Method 243.2 CLP-M) is recommended.

2. The following line may also be used: 403.1 nm Relative Sensitivity 10.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

NICKEL*

Method 249.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.3-5 mg/L using a wavelength of 232.0 nm
Sensitivity: 0.15 mg/L
Approximate Detection Limit: 0.04 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionizing distilled water. Add 10 mL of conc. nitric acid and dilute to 1 liter deionized distilled water. 1 mL = 1 mg Ni (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Interferences

1. The 352.4 nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For concentrations of nickel below 100 ug/L, use of the Furnace Technique (Method 249.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

SILVER*

Method 272.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-4 mg/L using a wavelength of 328.1 nm
Sensitivity: 0.06 mg/L
Approximate Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$, (analytical reagent grade) in deionized distilled water, add 10 mL conc. HNO_3 and make up to 1 liter. 1 mL = 1 mg Ag (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

3. Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide, KI (analytical reagent grade) in 50 mL of deionized distilled water, add 12.7 grams of iodine, I_2, (analytical reagent grade) and dilute to 100 mL. Store in a brown bottle.

4. Cyanogen Iodide (CNI) Solution: To 50 mL of deionized distilled water add 4.0 mL conc. NH_4OH, 6.5 grams KCN, and 5.0 mL of 1.0 N I_2 solution. Mix and dilute to 100 mL with deionized distilled water. Fresh solution should be prepared every two weeks.(1)

Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Notes

1. For concentrations of silver below 30 ug/L, use of the Furnace Technique (Method 272.2 CLP-M) is recommended.

2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/L are not stable over long periods of time.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

3. If absorption to container walls or the formation of AgCl is suspected, make the sample basic using conc. NH_4OH and add 1 mL of (CNI) solution per 100 mL of sample. Mix the sample and allow to stand for 1 hour before proceeding with the analysis.(1)

4. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 2.

THALLIUM*

Method 279.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-20 mg/L using a wavelength of 276.8 nm
Sensitivity: 0.5 mg/L
Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.303 g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Tl (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Thallium hollow cathode lamp
2. Wavelength: 276.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of thallium below 0.2 mg/L, use of the Furnace Technique (Method 279.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

VANADIUM*

Method 286.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 2-100 mg/L using a wavelength of 318.4 nm
Sensitivity: 0.8 mg/L
Approximate Detection Limit: 0.2 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade) in 10 mL of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg V (1000 mg/L).

2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 mL of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 mL.

3. Prepare dilutions of the stock vandium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 2 mL of the aluminum nitrate solution.

Instrumental Parameters (General)

1. Vanadium hollow cathode lamp
2. Wavelength: 318.4 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Interferences

1. It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards. [Talanta 15, 871 (1968)].

Notes

1. For concentrations of vanadium below 0.5 mg/L, use of the Furnace Technique (Method 282.6 CLP-M) is recommended.

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*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

ZINC*

Method 289.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.05-1 mg/L using a wavelength of 213.9 nm
Sensitivity: 0.02 mg/L
Approximate Detection Limit: 0.005 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 mL HNO_3. When solution is complete make up to 1 liter with deionized distilled water. 1 mL = 1 mg Zn (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. High levels of silicon may interfere.

2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.

3. The sensitivity may be increased by the use of low-temperature flames.

4. Some container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of the polypropylene caps is recommended.

5. For concentrations of zinc below 0.01 mg/L, use of the Furnace Technique (Method 289.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

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SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, September 1982.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures. NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze at least two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion spikes, duplicates,

serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (ICV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

Sensitivity, instrumental detection limits (IDL's), precision, linear dynamic range and interference effects must be established for each analyte on a particular instrument. All reported measurements must be within the instrumental linear ranges. The analyst must maintain quality control data confirming instrument performance and analytical results.

In addition, the Contractor shall establish a quality assurance program with the objective of providing sound analytical chemical measurements. This program shall incorporate the quality control procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

As evidence of such a program, the Contractor shall prepare a written Quality Assurance Plan (QAP) (see Section III) which describes the procedures that are implemented to achieve the following:

Maintain data integrity, validity, and useability.

Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility.

Detect problems through data assessment and establishes corrective action procedures which keep the analytical process reliable.

Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

SECTION III

QUALITY ASSURANCE PLAN

The QAP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA and QC activities designed to achieve the data quality requirements in this contract. Where applicable, SOPs pertaining to each element shall be included or referenced as part of the QAP. The QAP must be available during on-site laboratory evaluation and upon written request by the APO. The elements of the QAP are listed in the following outline.

A. Organization and Personnel

1. QA Policy and Objectives

2. QA Management

   a. Organization

   b. Assignment of QC and QA Responsibilities

   c. Reporting Relationships

   d. QA Document Control Procedures

   e. QA Program Assessment Procedures

3. Personnel

   a. Resumes

   b. Education and Experience Pertinent to this Contract

   c. Training Progress

B. Facilities and Equipment

1. Instrumentation and Backup Alternatives

2. Maintenance Activities and Schedules

C. Document Control

1. Laboratory Notebook Policy

2. Samples Tracking/Custody Procedures

3. Logbook Maintenance and Archiving Procedures

4. SDG File Organization, Preparation and Review Procedures

5. Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs

6. Process for Revision of Technical or Documentation Procedures

D. Analytical Methodology

1. Calibration Procedures and Frequency

2. Sample Preparation Procedures

3. Sample Analysis Procedures

4. Standards Preparation Procedures

5. Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

E. Data Generation

1. Data Collection Procedures

2. Data Reduction Procedures

3. Data Validation Procedures

4. Data Reporting and Authorization Procedures

F. Quality Assurance

1. Data Quality Assurance

2. Systems/Internal Audits

3. Performance/External Audits

4. Corrective Action Procedures

5. Quality Assurance Reporting Procedures

6. Responsibility Designation

G. Quality Control

1. Solvent, Reagent and Adsorbent Check Analysis

2. Reference Material Analysis

3. Internal Quality Control Checks

4. Corrective Action and Determination of QC Limit Procedures

5. Responsibility Designation

Updating and Submission of the QAP:

Within 60 Days of contract award:

During the contract solicitation process, the Contractor was required to submit their QAP to EMSL/LV and NEIC. Within sixty (60) days after contract award, the Contractor shall send a revised QAP, fully compliant with the requirements of this contract, to the Technical Project Officer, EMSL/LV and NEIC. The revised QAP will become the official QAP under the contract. The revised QAP must include:

1) Changes resulting from A) The Contractor's internal review of their organization, personnel, facility, equipment, policy and procedures and B) The Contractor's implementation of the requirements of the contract; and,

2) Changes resulting from the Agency's review of the laboratory evaluation sample data, bidder supplied documentation, and recommendations made during the pre-award On-Site laboratory evaluation

Subsequent submissions:

During the term of contract, the Contractor shall amend the QAP when the following circumstances occur:

1) The Agency modifies the contract,

2) The Agency notifies the Contractor of deficiencies in the QAP document

3) The Agency notifies the Contractor of deficiencies resulting from the Agency's review of the Contractor's performance,

4) The Contractor identifies deficiencies resulting from their internal review of their QAP document,

5) The Contractor's organization, personnel, facility, equipment, policy or procedures change,

6) The Contractor identifies deficiencies resulting from the internal review of their organization, personnel, facility, equipment, policy or procedures changes.

The Contractor shall amend the QAP within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the QAP and what is presently occurring at the Contractor's facility.

When the QAP is amended, all changes in the QAP must be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, or highlighting the change by underlining the change, bold printing the change, or using a different print font). The amended section pages must have the date on which the changes were implemented. The Contractor shall incorporate all amendments to the current QAP document. The Contractor shall archive all amendments to the QAP document for future reference by the Agency.

The Contractor shall send a copy of the current QAP document within 14 days of a request by the Technical Project Officer or Administrative Project Officers to the designated recipients.

Corrective Action:

If a Contractor fails to adhere to the requirements listed in this section, a Contractor may expect, but the Agency is not limited to the following actions: reduction of numbers of samples sent under this contract, suspension of sample shipment to the Contractor, data package audit, an On-Site laboratory evaluation, remedial performance evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION IV

STANDARD OPERATING PROCEDURES

In order to obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of Standard Operating Procedures (SOPs). As defined by the EPA, an SOP is a written document which provides directions for the step-by-step execution of an operation, analysis, or action which is commonly accepted as the method for performing certain routine or repetitive tasks.

SOPs prepared by the Contractor must be functional: i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts. All SOPs, as presented to the Agency, must reflect activities as they are currently performed in the laboratory. In addition, all SOPs must be:

- Consistent with current EPA regulations, guidelines, and the CLP contract's requirements.
- Consistent with instruments manufacturers's specific instruction manuals.
- Available to the EPA during an On-Site Laboratory Evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During On-Site Laboratory evaluations, laboratory personnel may be asked to demonstrate the application of the SOPs.
- Capable of providing for the development of documentation that is sufficiently complete to record the performance of all tasks required by the protocol.
- Capable of demonstrating the validity of data reported by the Contractor and explain the cause of missing or inconsistent results.
- Capable of describing the corrective measures and feedback mechanism utilized when analytical results do not meet protocol requirements.
- Reviewed regularly and updated as necessary when contract, facility, or Contractor procedural modifications are made.
- Archived for future reference in usability or evidentiary situations.
- Available at specific work stations as appropriate
- Subject to a document control procedure which precludes the use of outdated or inappropriate SOPs.

SOP FORMAT:

The format for SOPs may vary depending upon the kind of activity for which they are prepared, however, at a minimum, the following sections must be included:

- Title Page

- o Scope and Application
- o Definitions
- o Procedures
- o QC Limits
- o Corrective Action Procedures, Including Procedures for Secondary Review of Information Being Generated
- o Documentation Description and Example Forms
- o Miscellaneous Notes and Precautions
- o References

SOPS REQUIRED:

The following SOPs are required by the Agency:

1. Evidentiary SOP

   Evidentiary SOPs for required chain-of-custody and document control are discussed in Exhibit F

2. Sample Receipt and Storage
   a. Sample receipt and identification logbooks
   b. Refrigerator temperature logbooks
   c. Security precautions
3. Sample preparation
4. Glassware cleaning
5. Calibration (Balances, etc.)
   a. Procedures
   b. Frequency requirements
   c. Preventative maintenance schedule and procedures
   d. Acceptance criteria and corrective actions
   e. Logbook maintenance authorization
6. Analytical procedures (for each analytical system)
   a. Instrument performance specifications
   b. Instrument operating procedures
   c. Data acquisition system operation
   d. Procedures when automatic quantitation algorithms are overridden
   e. QC required parameters
   f. Analytical run/injection logbooks
   g. Instrument error and editing flag descriptions and resulting corrective actions

7. Maintenance activities (for each analytical system)
   a. Preventative maintenance schedule and procedures
   b. Corrective maintenance determinants and procedures
   c. Maintenance authorization
8. Analytical standards
   a. Standard coding/identification and inventory system
   b. Standards preparation logbook(s)
   c. Standard preparation procedures
   d. Procedures for equivalency/traceability analyses and documentation
   e. Purity logbook (primary standards and solvents)
   f. Storage, replacement, and labelling requirements
   g. QC and corrective action measures
9. Data reduction procedures
   a. Data processing systems operation
   b. Outlier identification methods
   c. Identification of data requiring corrective action
   d. Procedures for format and/or forms for each operation
10. Documentation policy/procedures
   a. Laboratory/analyst's notebook policy, including review policy
   b. Complete SDG File contents
   c. Complete SDG File organization and assembly procedures, including review policy
   d. Document inventory procedures, including review policy
11. Data validation/self inspection procedures
   a. Data flow and chain-of-command for data review
   b. Procedures for measuring precision and accuracy
   c. Evaluation parameters for identifying systematic errors
   d. Procedures to assure that hardcopy and diskette deliverables are complete and compliant with the requirements in SOW Exhibits B and H.
   e. Procedures to assure that hardcopy deliverables are in agreement with their comparable diskette deliverables.
   f. Demonstration of internal QA inspection procedure (demonstrated by supervisory sign-off on personal notebooks, internal laboratory evaluation samples, etc.).
   g. Frequency and type of internal audits (eg., random, quarterly, spot checks, perceived trouble areas).

h. Demonstration of problem identification-corrective actions and resumption of analytical processing. Sequence resulting from internal audit (i.e., QA feedback).

i. Documentation of audit reports, (internal and external), response, corrective action, etc.

12. Data management and handling

a. Procedures for controlling and estimating data entry errors.

b. Procedures for reviewing changes to data and deliverables and ensuring traceability of updates.

c. Lifecycle management procedures for testing, modifying and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems.

d. Database security, backup and archival procedures including recovery from system failures.

e. System maintenance procedures and response time.

f. Individuals(s) responsible for system operation, maintenance, data integrity and security.

g. Specifications for staff training procedures.

SOPS DELIVERY REQUIREMENTS:

Updating and submission of SOPs:

Within 60 days of contract award:

During the contract solicitation process, the Contractor was required to submit their SOPs to EMSL/LV and NEIC. Within sixty (60) days after contract award, the Contractor shall send a complete revised set of SOPs, fully compliant with the requirements of this contract, to the Technical Project Officer, EMSL/LV and NEIC. The revised SOP's will become the official SOPs under the contract. The revised SOPs must include:

1) Changes resulting from A) the Contractor's internal review of their procedures and B) the Contractor's implementation of the requirements of the contract;

2) Changes resulting from the Agency's review of the laboratory evaluation sample data, bidder supplied documentation, and recommendations made during the pre-award On-Site laboratory evaluation.

Subsequent Submissions:

During the term of contract, the Contractor shall amend the SOPs when the following circumstances occur:

1) The Agency modifies the contract,

2) The Agency notifies the Contractor of deficiencies in their SOPs documentation

3) The Agency notifies the Contractor of deficiencies resulting from the Agency's review of the Contractor's performance,

4) The Contractor's procedures change,

5) The Contractor identifies deficiencies resulting from the internal review of their SOPs documentation, or

6) The Contractor identifies deficiencies resulting form the internal review of their procedures.

The SOPs must be amended or new SOPs must be written within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Contractor's facility. All changes in the SOPs must be clearly marked (e.g., a bar in the margin indicating where the change is in the document, or highlighting the change by underlining the change, bold printing the change, or using a different print font). The amended/new SOPs must have the date on which the changes were implemented.

When the SOPs are amended or new SOPs are written, the Contractor shall document in a letter the reasons for the changes, and submit the amended SOPs or new SOPs to the Technical Project Officer, EMSL/LV (quality assurance/technical SOPs) and NEIC (evidentiary SOPs). The Contractor shall send the letter and the amended sections of the SOPs or new SOPs within 14 days of the change. An alternate delivery schedule for the submittal of the letter and amended/new SOPs may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer/Administrative Project Officer will not grant an extension for greater than 30 days for amending/writing new SOPs. The Technical Project Officer/Administrative Project Officer will not grant an extension for greater than 14 days for submission of the letter documenting the reasons for the changes and for submitting amended/new SOPs. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

The Contractor shall send a complete set of current SOPs within 14 days of a request by the Technical Project Officer or Administrative Project Officer to the recipients he/she designates.

Corrective action:

If a Contractor fails to adhere to the requirements listed in this section, a Contractor may expect, but the Agency is not limited to the following action: reduction of number of samples sent under this contract, suspension of sample shipment to the Contractor, data package audit, On-Site laboratory evaluation, remedial performance evaluation sample, and/or contract sanction, such as a Cure Notice.

SECTION V

REQUIRED QA/QC OPERATIONS

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. ICP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh daily or each time an analysis is to be made and discarded after use. For atomic absorption systems, prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be

within 5% of the true value. Each standards concentration and the calculations to show that the 5% criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The 5% criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by compliant CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that

particular ICV. The values for the initial and subsequent continuing calibration verification shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NIST Standards
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set) Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch[1] of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.

2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The

   sample concentration is not to be corrected for the blank value.

3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EMSL/LV) if available and analyzed according to the instructions supplied with the ICS.

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[1] A group of samples prepared at the same time.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of ±20% of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of ±20% of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.[2]

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. Note: See Table 3 footnotes for concentration levels and applications. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

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[2]EPA may require additional spike sample analysis, upon Administrative Project Officer request, for which the Contractor will be paid.

$$\%\text{Recovery} = \frac{(SSR-SR)}{SA} \times 100$$

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

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., ug/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

	For ICP/AA		For Furnace AA		Other[1][2]
Element	Water (ug/L)	Soil[2] (mg/kg)	Water (ug/L)	Soil[2] (mg/kg)	
Aluminum	2,000	*			
Antimony	500	100	100	20	
Arsenic	2,000	400	40	8	
Barium	2,000	400			
Beryllium	50	10			
Cadmium	50	10	5	1	
Calcium	*	*			
Chromium	200	40			
Cobalt	500	100			
Copper	250	50			
Iron	1,000	*			
Lead	500	100	20	4	
Magnesium	*	*			
Manganese	500	100			
Mercury					1
Nickel	500	100			
Potassium	*	*			
Selenium	2,000	400	10	2	
Silver	50	10			
Sodium	*	*			
Thallium	2,000	400	50	10	
Vanadium	500	100			
Zinc	500	100			
Cyanide					100[3]

*No spike required. NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

[1]Spiking level reported is for both water and soil/sediment matrices.

[2]The levels shown indicate concentrations in the final digestate of the spiked sample (100 mL for mercury and 200 mL for all other metals) when the wet weight of 1 gram (for ICP, Furnace, and Flame AA), or 0.2 grams

(for mercury) of sample is taken for analysis. Adjustment must be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment must be made for microwave digestion procedure where 0.5 grams of sample or 50.0 mL (45.0 mL of sample plus 5.0 mL of acid) of aqueous sample are required for analysis.

[3]The level shown indicates the amount of cyanide that must be added to the original (undistilled) sample. For instance, 100 ug must be added per each Liter of aqueous sample. If the sample volume is 500 mL, then 50 ug of cyanide must be added. If the volume is 50 mL, then 5 ug of cyanide must be added.
For soil samples, 25 ug of cyanide must be added per each gram of solid sample taken for analysis. The spiking level is dependent on the weight of the sample taken and the final distillate volume. If one gram of sample is taken for analysis, and the final distillate volume is 250 mL, then the distillate must contain cyanide at a concentration of 100 ug/L. If five grams of sample are taken, then the distillate must contain cyanide at a concentration of 500 ug/L. Assuming a sample of one gram, the manual and semi-automated colorimetric methods call for a cyanide concentration of 25 ug per the 500 mL mixture of the sample, reagents, and water before distillation. The final distillate, in this case, contains cyanide at a concentration of 100 ug/L. For the midi-distillation method, a cyanide concentration of 25 ug must be added into the 50 mL mixture of sample, reagents, and water before distillation. This yields a cyanide concentration of 500 ug/L in the final distillate of 50 mL.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.[3] Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

[3]EPA may require additional duplicate sample analyses, upon Administrative Project Officer request, for which the Contractor will be paid.

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of (±) the CRDL must be used if either the sample or duplicate value is less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the ± CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results < 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I = Initial Sample Result
S = Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within 5% of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of standard addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation

(CV). Average concentration values are used for reporting purposes. The Contractor must be consistent per method and SDG in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Contractor must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I- IN for that sample.

b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike[4] will be required to be at a concentration (in the sample) 2x CRDL (except for lead which must be at 20 ug/L). This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.

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[4]Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

2) If the spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"[5], report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "W".

3) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is at or between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

4) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

c. The following procedures will be incorporated into MSA analyses.

1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.

4) Spikes must be prepared such that:

a) Spike 1 is approximately 50% of the sample concentration.

b) Spike 2 is approximately 100% of the sample concentration.

c) Spike 3 is approximately 150% of the sample concentration.

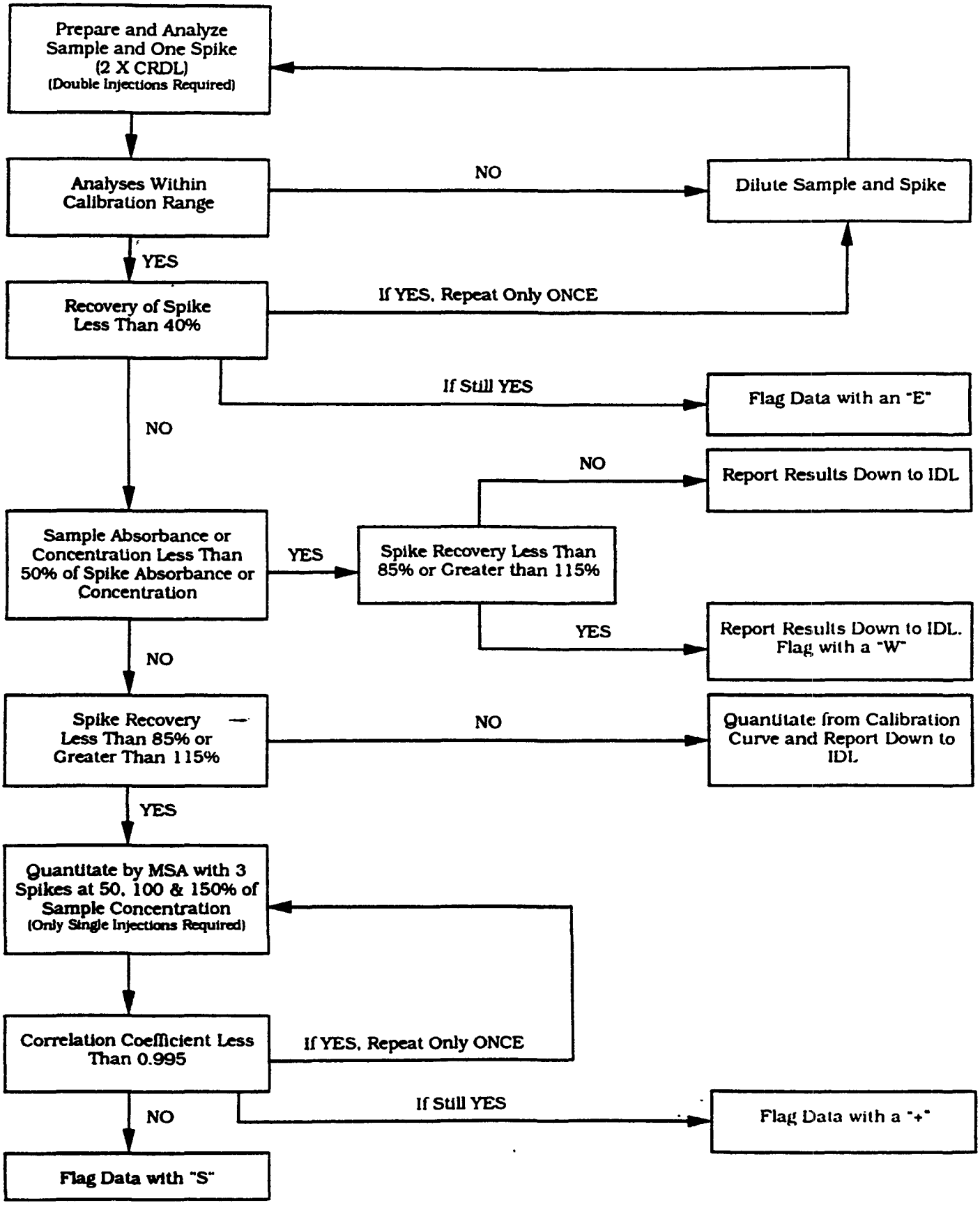
5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA

[5]"Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.

6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Figure 1.
Furnace Atomic Absorption Analysis Scheme



SECTION VI

CONTRACT COMPLIANCE SCREENING

Contract Compliance Screening (CCS) is one aspect of the Government's contractual right of inspection of analytical data. CCS examines the Contractor's adherence to the contract requirements based on the sample data package delivered to the Agency.

CCS is performed by the Sample Management Office (SMO) under the direction of the EPA. To assure a uniform review, a set of standardized procedures have been developed to evaluate the sample data package submitted by a Contractor against the technical and completeness requirements of the contract.

CCS results are mailed to the Contractor and all other data recipients. The Contractor has a period of time to correct deficiencies. The Contractor must send all corrections to the Regional Client, EMSL/LV, and SMO.

CCS results are used in conjunction with other information to measure overall Contractor performance and to take appropriate actions to correct deficiencies in performance.

The Agency may generate a CCS trend report which summarizes CCS results over a given period of time. The Agency may send the CCS trend report or discuss the CCS trend report during an On-Site laboratory evaluation. In a detailed letter to the Technical Project Officer and Administrative Project Officer, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the On-Site laboratory evaluation. An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented by the Technical Project Officer or Administrative Project Officer to approve or disprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer <u>will not</u> grant an extension for greater than 14 days for the Contractor's response to the CCS trend report.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section IV.

If the Contractor fails to adhere to the requirements listed in this section, the Contractor may expect, but the Agency is not limited to the following actions: reduction of number of samples sent under the contract, suspension of sample shipment to the Contractor, data package audit, an On-Site laboratory evaluation, a remedial performance evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION VII

ANALYTICAL STANDARD REQUIREMENTS

The U.S. Environmental Protection Agency may be unable to supply analytical reference standards either for direct analytical measurements or for the purpose of traceability. In these cases, all contract laboratories will be required to prepare from materials or purchase from private chemical supply houses those standards necessary to successfully and accurately perform the analyses required in this protocol.

A. Preparation of Chemical Standards from the Neat High Purity Bulk Material

If the laboratory cannot obtain analytical reference data from the USEPA, the laboratory may prepare their own chemical standards. Laboratories should obtain the highest purity possible when purchasing chemical standards; standards purchased at less than 97% purity must be documented as to why a higher purity could not be obtained.

1. If required by the manufacturer, the chemical standards must be kept refrigerated when not being used in the preparation of standard solutions. Proper storage of chemicals is essential in order to safeguard them from decomposition.

2. The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration of solute in a solution standard, it is the contract laboratory's responsibility to have analytical documentation ascertaining that the purity of each compound is correctly stated. Purity confirmation, when performed, should use appropriate techniques. Use of two or more independant methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

Equation 1

$$\text{weight of impure compound} = \frac{\text{weight of pure compound}}{(\text{percent purity}/100)}$$

where "weight of pure compound" is that required to prepare a specific volume of a solution standard of a specified concentration.

3. Mis-identification of compounds occasionally occurs and it is possible that a mislabeled compound may be received from a chemical supply house. It is the contract laboratory's responsibility to have analytical documentation ascertaining that all compounds used in the preparation of solution standards be correctly identified.

4. Log notebooks are to be kept for all weighing and dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be recorded and verified by a second person. All solution standards

are to be refrigerated, if required, when not in use. All solution standards are to be clearly labeled as to the identity of the analyte or analytes, concentration, date prepared, solvent, and initials of the preparer.

B. Purchase of chemical standards already in solution

1. Solutions of analytical reference standards can be purchased by Contractors provided they meet the following criteria:

   Laboratories must maintain documentation of the purity confirmation of the material to verify the integrity of the standard solutions they purchase.

2. The Contractor must purchase standards for which the quality is demonstrated statistically and analytically by a method of the supplier's choice. One way this can be demonstrated is to prepare and analyze three solutions; a high standard, a low standard, and a standard at the target concentration (see parts a and b below). The supplier must then demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations. This is done by the Student's t-test in part "d". If this is achieved, the supplier must then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards. This is done by the Student's t-test in part e. Thus the standard is certified to be within 10 percent of the target concentration.

   If the procedure above is used, the supplier must document that the following have been achieved:

   a. Two solutions of identical concentration must be prepared independently from neat materials. An aliquot of the first solution must be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration ten percent greater than the target standard. This is called the "high standard". One further aliquot is taken from the second solution and diluted to a concentration 10 percent less than the target standard. This is called the "low standard".

   b. Six replicate analyses of each standard (a total of 18 analyses) must be performed in the following sequence: low standard, target, high standard, low standard, target standard, high standard, ...

   c. The mean and variance of the six results for each solution must be calculated.

   Equation 2

   $$\text{MEAN} = (Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6)/6$$

Equation 3

$$\text{VARIANCE}_2 = (Y_1^2 + Y_2^2 + Y_3^2 + Y_4^2 + Y_5^2 + Y_6^2 - (6*\text{MEAN})^2)/5$$

The values Y_1, Y_2, Y_3, ..., represent the results of the six analyses of each standard. The means of the low, target, and high standards are designated M_1, M_2, and M_3, respectively. The variances of the low, target, and high standards are designated V_1, V_2, and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

Equation 4

$$V_p = (V_1/(0.81) + V_2 + V_3/(1.21))/3$$

If the square root of V_p is less than one percent of M_2, then $M_2^2/10{,}000$ is to be used as the value of V_p in all subsequent calculations.

d. The test statistic must be calculated:

Equation 5

$$\text{TEST STATISTIC} = |(M_3/1.1) - (M_1/0.9)|/(V_p/3)^{0.5}$$

If the test statistic exceeds 2.13 then the supplier has failed to demonstrate a twenty percent difference between the high and low standards. In such a case, the standards are not acceptable.

e. The test statistic must be calculated:

Equation 6

$$\text{TEST STATISTIC} = |M_2 - (M_1/1.8) - (M_3/2.2)|/(V_p/4)^{0.5}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate that the target standard concentration is midway between the high and low standards. In such a case, the standards are not acceptable.

f. The 95 percent confidence intervals for the mean result of each standard must be calculated:

Equation 7

$$\text{Interval for Low Standard} = M_1 \pm (2.13)(V_p/6)^{0.5}$$

Equation 8

$$\text{Interval for Target Standard} = M_2 \pm (2.13)(V_p/6)^{0.5}$$

Equation 9

$$\text{Interval for High Standard} = M_3 \pm (2.13)(V_p/6)^{0.5}$$

These intervals must not overlap. If overlap is observed, then the supplier has failed to demonstrate the ability to discriminate the 10 percent difference in concentrations. In such a case, the standards are not acceptable.

In any event, the laboratory is responsible for the quality of the standards employed for analyses under this contract.

C. Requesting Standards From the EPA Standards Repository

Solutions of analytical reference materials can be ordered from the U.S. EPA Chemical Standards Repository, depending on availability. The Contractor can place an order for standards only after demonstrating that these standards are not available from commercial vendors either in solution or as a neat material.

D. Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of each laboratory to maintain the necessary documentation to show that the chemical standards they have used in the performance of CLP analysis conform to the requirements previously listed. Weighing logbooks, calculations, raw data, etc., whether produced by the laboratory or purchased from chemical supply houses, must be maintained by the laboratory and may be subject to review during On-Site inspection visits. In those cases where the documentation is supportive of the analytical results of data packages sent to EPA, such documentation is to be kept on file by the laboratories for a period of one year.

Upon request by the Technical Project Officer or Administrative Project Officer, the Contractor shall submit their most recent previous year's documentation (12 months) for the verification and preparation of chemical standards within 14 days of the receipt of request to the recipients he/she designates.

The Agency may generate a report discussing deficiencies in the Contractor's documentation for the verification and preparation of chemical standards or may discuss the deficiencies during an On-Site laboratory evaluation. In a detailed letter to the Technical Project Officer, Administrative Project Officer, and EMSL-LV, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the On-Site laboratory evaluation. An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer/Administrative Project Officer <u>will not</u> grant an extension for greater than 14 days for the Contractor's response letter to the standards documentation report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section IV.

If the Contractor fails to adhere to the requirements listed in Section VII, a Contractor may expect, but the Agency is not limited to the following actions: reduction of number of samples sent under the contract, suspension of sample shipment to Contractor, data package audit, an On-Site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION VIII

DATA PACKAGE AUDITS

Data package audits are performed by the Agency for program overview and specific Regional concerns. Standardized procedures have been established to assure uniformity of the auditing process. Data packages are periodically selected from recently received cases. They are evaluated for the technical quality of hardcopy raw data, quality assurance, and the adherence to contractual requirements. This function provides external monitoring of program QC requirements.

Data package audits are used to assess the technical quality of the data and evaluate overall laboratory performance. Audits provide the Agency with an in-depth inspection and evaluation of the Case data package with regard to achieving QA/QC acceptability. A thorough review of the raw data is completed including: all instrument readouts used for the sample results, chromatograms and other documentation for deviations from the contractual requirements, a check for transcription and calculation errors, a review of the qualifications of the laboratory personnel involved with the Case, and a review of all current SOPs on file.

Responding to the data package audit report:

After completion of the data package audit, the Agency may send a copy of the data package audit report to the Contractor or may discuss the data package audit report on an On-Site laboratory evaluation. In a detailed letter to the Technical Project Officer, Administrative Project Officer, and EMSL/LV, the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the report. An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and the Contracting Officer, why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer/Administrative Project Officer will not grant an extension for greater than 14 days for the Contractor's response letter to the data package report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section IV.

Corrective Actions

If the Contractor fails to adhere to the requirements listed in this section, the Contractor may expect, but the Agency is not limited to the following actions: reduction in the numbers of samples sent under the contract, suspension of sample shipment to the Contractor, an On-Site laboratory evaluation, data package audit, remedial performance evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION IX

PERFORMANCE EVALUATION SAMPLES

Although intralaboratory QC may demonstrate Contractor and method performance that can be tracked over time, an external performance evaluation program is an essential feature of a QA program. As a means of measuring Contractor and method performance, Contractors participate in interlaboratory comparison studies conducted by the EPA. Results from the analysis of these performance evaluation samples (PES) will be used by the EPA to verify the Contractor's continuing ability to produce acceptable analytical data. The results are also used to assess the precision and accuracy of the analytical methods for specific analytes.

Sample sets may be provided to participating Contractors as frequently as on an SDG-by-SDG basis as a recognizable QC sample of known composition; as a recognizable QC sample of unknown composition; or not recognizable as a QC material. The laboratory evaluation samples may be sent either by the Regional client or the National Program Office, and may be used for contract action.

Contractors are required to analyze the samples and return the data package and all raw data within the contract required turnaround time.

In addition to PES preparation and analysis, the Contractor will be responsible for correctly identifying and quantifying the analytes included in the PES. The Agency will notify the Contractor of unacceptable performance.

Contractors are required to analyze the samples and return the data package and all raw data within the contract required turnaround time.

A Contractor's results on the laboratory evaluation samples will determine the Contractor's performance as follows:

1. Acceptable, No Response Required (Score greater than or equal to 90 percent):

   Data meets most or all of the scoring criteria. No response is required.

2. Acceptable, Response Explaining Deficiency(ies) Required (Score greater than or equal to 75 percent but less than 90 percent):

   Deficiencies exist in the Contractor's performance.

   Within 14 days of receipt of notification from EPA, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Administrative Project Officer, the Technical Project Officer and EMSL/LV.

   An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve

or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer /Administrative Project Officer will not grant an extension for greater than 14 days for the Contractor's response letter to the laboratory evaluation sample report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section IV.

3. Unacceptable Performance, Response Explaining Deficiency(ies) Required (Score less than 75 percent):

Deficiencies exist in the Contractor's performance to the extent that the National Program Office has determined that the Contractor has not demonstrated the capability to meet the contract requirements.

Within 14 days of receipt of notification from EPA, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Administrative Project Officer, the Technical Project Officer and EMSL/LV.

An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer /Administrative Project Officer will not grant an extension for greater than 14 days for the Contractor's response letter to the performance evaluation sample report.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section IV.

The Contractor shall be notified by the Technical Project Officer or Administrative Project Officer concerning the remedy for their unacceptable performance. A Contractor may expect, but the Agency is not limited to, the following actions: reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, an On-Site laboratory evaluation, data package audit, remedial performance evaluation sample, and/or a contract sanction, such as a Cure Notice.

Note: A Contractor's prompt response demonstrating that corrective actions have been taken to ensure the Contractor's capability to meet contract requirements may facilitate continuation of full sample delivery.

If the Contractor fails to adhere to the requirements listed in this section, a Contractor may expect, but the Agency is not limited to the following actions: reduction in the number of samples sent under the contract, suspension of sample shipment to the Contractor, an On-Site laboratory evaluation, data package audit, a remedial laboratory evaluation sample and/or contract sanctions, such as a Cure Notice.

SECTION X

ON-SITE LABORATORY EVALUATIONS

At a frequency dictated by a contract laboratory's performance, the Administrative Project Officer, Technical Project Officer or their authorized representative will conduct an On-Site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Contractor's ability to meet selected terms and conditions specified in the contract. The evaluation process incorporates two separate categories: Quality Assurance Evaluation, and an Evidentiary Audit.

A. Quality Assurance On-Site Evaluation

Quality assurance evaluators inspect the Contractor's facilities to verify the adequacy and maintenance of instrumentation, the continuity of personnel meeting experience or education requirements, and the acceptable performance of analytical and QC procedures. The Contractor should expect that items to be monitored will include, but not be limited to the following:

- o Size and appearance of the facility
- o Quantity, age, availability, scheduled maintenance and performance of instrumentation
- o Availability, appropriateness, and utilization of the QAP and SOPs
- o Staff qualifications, experience, and personnel training programs
- o Reagents, standards, and sample storage facilities
- o Standard preparation logbooks and raw data
- o Bench sheets and analytical logbook maintenance and review
- o Review of the Contractor's sample analysis/data package inspection/data management procedures

Prior to an On-Site evaluation, various documentation pertaining to performance of the specific Contractor is integrated in a profile package for discussion during the evaluation. Items that may be included are previous On-Site reports, performance evaluation sample scores, Regional review of data, Regional QA materials, data audit reports, results of CCS, and data trend reports.

B. Evidentiary Audit

Evidence auditors conduct an On-Site laboratory evaluation to determine if laboratory policies and procedures are in place to satisfy evidence handling requirements as stated in Exhibit F. The evidence audit is comprised of the following three activities:

1. Procedural Audit

The procedural audit consists of review and examination of actual standard operating procedures and accompanying documentation for the following laboratory operations: sample receiving, sample

storage, sample identification, sample security, sample tracking (from receipt to completion of analysis) and analytical project file organization and assembly.

2. Written SOPs Audit

The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis) and analytical project file organization and assembly.

3. Analytical Project File Evidence Audit

The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

- o The accuracy of the document inventory
- o The completeness of the file
- o The adequacy and accuracy of the document numbering system
- o Traceability of sample activity
- o Identification of activity recorded on the documents
- o Error correction methods

C. Discussion of the On-Site Team's Findings

The quality assurance and evidentiary auditors discuss their findings with the Administrative Project Officer/Technical Project Officer prior to debriefing the Contractor. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Contractor personnel.

D. Corrective Action Reports For Follow-Through to Quality Assurance and Evidentiary Audit Reports

On-site laboratory evaluation:

Following an On-Site laboratory evaluation, quality assurance and/or evidentiary audit reports which discuss deficiencies found during the On-Site evaluation may be sent to the Contractor. In a detailed letter, the Contractor shall discuss the corrective actions implemented to resolve the deficiencies discussed during the On-Site evaluation and discussed in the report(s) to the Technical Project Officer, Administrative Project Officer, and EMSL/LV (response to quality assurance/technical report) and NEIC (response to the evidentiary report), within 14 days of receipt of the report. An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical

Project Officer, Administrative Project Officer, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer/Administrative Project Officer will not grant an extension for greater than 14 days for the Contractor's response letter to the quality assurance and evidentiary audit report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section IV.

Corrective actions

If the Contractor fails to adhere to the requirements listed in this section, the Contractor may expect, but the Agency is not limited to the following actions: reduction in the number of samples sent under the contract, suspension of sample shipment to the Contractor, an On-Site laboratory evaluation, data package audit, a remedial performance evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION XI

DATA MANAGEMENT

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage and security of computer readable data and files. These procedures should be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security), documentation operations, traceability and quality control.

Data manually entered from hard-copy must be quality controlled and the error rates estimated. Systems should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates must be estimated and recorded on a monthly basis by reentering a statistical sample of the data entered and calculating discrepancy rates by data element.

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted must be documented to allow traceablilty of updates. Documentation must include the following for each change:

- Justification or rationale for the change.
- Initials of the person making the change or changes. Data changes must be implemented and reviewed by a person or group independant of the source generating the deliverable.
- Change documentation must be retained according to the schedule of the original deliverable.
- Resubmitted diskettes or other deliverables must be reinspected as a part of the laboratories' internal inspection process prior to resubmission. The entire deliverable, not just the changes, must be inspected.
- The Laboratory Manager must approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by laboratory auditors.

Lifecycle management procedures must be applied to computer software systems developed by the laboratory to be used to generate and edit contract deliverables. Such systems must be thoroughly tested and documented prior to utilization.

- A software test and acceptance plan including test requirements, test results and acceptance criteria must be developed, followed, and available in written form.
- System changes must not be made directly to production systems generating deliverables. Changes must be made first to a development system and tested prior to implementation.
- Each version of the production system will be given an identification number, date of installation, date of last operation and archived.

- System and operations documentation must be developed and maintained for each system. Documentation must include a users manual and an operations and maintenance manual.

Individual(s) responsible for the following functions must be identified:

- System operation and maintenance including documentation and training.
- Database integrity, including data entry, data updating and quality control.
- Data and system security, backup and archiving.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND STANDARD OPERATING PROCEDURES

1. SAMPLE CHAIN-OF-CUSTODY

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To accomplish this, Contractors are required to develop and implement the following sample identification, chain-of-custody, sample receiving, and sample tracking procedures.

1.1 Sample Identification

To assure traceability of the samples while in possession of the Contractor, the Contractor shall have a specified method for maintaining identification of samples throughout the laboratory.

Each sample and sample preparation container shall be labeled with the EPA number or a unique laboratory identifier. If a unique laboratory identifier is used, it shall be cross-referenced to the EPA number.

1.2 Chain-of-Custody Procedures

Because of the nature of the data being collected, the custody of EPA samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. The Contractor shall have procedures ensuring that EPA sample custody is maintained and documented. A sample is under custody if:

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

1.3 Sample Receiving Procedures

1.3.1 The Contractor shall designate a sample custodian responsible for receiving all samples.

1.3.2 The Contractor shall designate a representative to receive samples in the event that the sample custodian is not available.

1.3.3 The condition of the shipping containers and sample bottles shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.4 The condition of the custody seals (intact/not intact) shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.5 The sample custodian or his/her representative shall check for the presence or absence of the following documents accompanying the sample shipment:

- o Airbills or airbill stickers
- o Custody seals
- o EPA custody records
- o EPA traffic reports or SAS packing lists
- o Sample tags

1.3.6 The sample custodian or his/her representative shall sign and date all forms (e.g., custody records, traffic reports or packing lists, and airbills) accompanying the samples at the time of sample receipt.

1.3.7 The Contractor shall contact the Sample Management Office (SMO) to resolve discrepancies and problems such as absent documents, conflicting information, broken custody seals, and unsatisfactory sample condition (e.g., leaking sample bottle).

1.3.8 The Contractor shall record the resolution of discrepancies and problems on Telephone Contact Logs.

1.3.9 The following information shall be recorded on Form DC-1 (See Exhibit B) by the sample custodian or his/her representative as samples are received and inspected:

- o Condition of the shipping container
- o Presence or absence and condition of custody seals on shipping and/or sample containers
- o Custody seal numbers, when present
- o Condition of the sample bottles
- o Presence or absence of airbills or airbill stickers
- o Airbill or airbill sticker numbers
- o Presence or absence of EPA custody records
- o Presence or absence of EPA traffic reports or SAS packing lists
- o Presence or absence of sample tags
- o Sample tag identification numbers cross-referenced to the EPA sample numbers
- o Verification of agreement or non-agreement of information recorded on shipping documents and sample containers
- o Problems or discrepancies

1.4 Sample Tracking Procedures

The Contractor shall maintain records documenting all phases of sample handling from receipt to final analysis.

2. DOCUMENT CONTROL PROCEDURES

The goal of the laboratory document control program is to assure that all documents for a specified Sample Delivery Group (SDG) will be accounted for when the project is completed. Accountable documents used by contract laboratories shall include, but not be limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses. The following document control procedures have been established to assure that all laboratory records are assembled and stored for delivery to EPA or are available upon request from EPA prior to the delivery schedule.

2.1 Preprinted Laboratory Forms and Logbooks

2.1.1 All documents produced by the Contractor which are directly related to the preparation and analysis of EPA samples shall become the property of the EPA and shall be placed in the complete sample delivery group file (CSF). All observations and results recorded by the laboratory but not on preprinted laboratory forms shall be entered into permanent laboratory logbooks. When all data from a SDG is compiled, all original laboratory forms and copies of all SDG-related logbook entries shall be included in the documentation package.

2.1.2 The Contractor shall identify the activity recorded on all laboratory documents which are directly related to the preparation and analysis of EPA samples.

2.1.3 Pre-printed laboratory forms shall contain the name of the laboratory and be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.4 Logbook entries shall be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.5 Logbook entries shall be in chronological order. Entries in logbooks, with the exception of instrument run logs and extraction logs, shall include only one SDG per page.

2.1.6 Pages in both bound and unbound logbooks shall be sequentially numbered.

2.1.7 Instrument run logs shall be maintained so as to enable a reconstruction of the run sequence of individual instruments.

Because the laboratory must provide copies of the instrument run logs to EPA, the laboratory may exercise the option of using only laboratory or EPA sample identification numbers in the logs for sample ID rather than government agency or commercial client names to preserve the confidentiality of commercial clients.

2.1.8 Corrections to supporting documents and raw data shall be made by drawing a single line through the error and entering the correct information. Corrections and additions to supporting documents and raw data shall be dated and initialed. No information shall be obliterated or rendered unreadable.

All notations shall be recorded in ink.

Unused portions of documents shall be "z'd" out.

2.2 Consistency of Documentation

The Contractor shall assign a document control officer responsible for the organization and assembly of the CSF.

All copies of laboratory documents shall be complete and legible.

Original documents which include information relating to more than one SDG shall be filed in the CSF of the lowest SDG number. The copy(s) shall be placed in the other CSF(s) and the Contractor shall record the following information on the copy(s) in red ink:

"COPY

ORIGINAL IS FILED IN CSF _____"

The Contractor shall sign and date this addition to the copy(s).

Before releasing analytical results, the document control officer shall assemble and cross-check the information on samples tags, custody records, lab bench sheets, personal and instrument logs, and other relevant deliverables to ensure that data pertaining to each particular sample or sample delivery group is consistent throughout the CSF.

2.3 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in the CSF shall be inventoried and assigned a serialized number as described in Exhibit B).

All documents relevant to each sample delivery group, including logbook pages, bench sheets, mass spectra, chromatograms, screening records, re-preparation records, re-analysis records, records of failed or attempted analysis, custody records, library research results, etc. shall be inventoried.

The Document Control Officer (DCO) shall be responsible for ensuring that all documents generated are placed in the CSF for inventory and are delivered to the appropriate EPA region or other receiver as designated by EPA. The DCO shall place the sample tags in plastic bags in the file.

2.4 Storage of EPA Files

The Contractor shall maintain EPA laboratory documents in a secure location.

2.5 Shipment of Deliverables

The Contractor shall document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that they cannot be opened without damaging or breaking the seal. The Contractor shall document what was sent, to whom, the date, and the method (carrier) used.

A copy of the transmittal letter for the CSF shall be sent to the NEIC/CEAT and the SMO.

3. SPECIFICATIONS FOR WRITTEN STANDARD OPERATING PROCEDURES

The Contractor shall have written standard operating procedures (SOPs) for receipt of samples, maintenance of custody, sample identification, sample storage, sample tracking, and assembly of completed data.

An SOP is defined as a written narrative stepwise description of laboratory operating procedures including examples of laboratory documents. The SOPs shall accurately describe the actual procedures used in the laboratory, and copies of the written SOPs shall be available to the appropriate laboratory personnel. These procedures are necessary to ensure that analytical data produced under this contract are acceptable for use in EPA enforcement case preparation and litigation. The Contractor's SOPs shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA as the basis for laboratory evidence audits.

3.1 The Contractor shall have written SOPs describing the sample custodian's duties and responsibilities.

3.2 The Contractor shall have written SOPs for receiving and logging in of the samples. The procedures shall include but not be limited to documenting the following information:

3.2.1 Presence or absence of EPA chain-of-custody forms

3.2.2 Presence or absence of airbills or airbill stickers

3.2.3 Presence or absence of traffic reports or SAS packing lists

3.2.4 Presence or absence of custody seals on shipping and/or sample containers and their condition

3.2.5 Custody seal numbers, when present

3.2.6 Airbill or airbill sticker numbers

3.2.7 Presence or absence of sample tags

3.2.8 Sample tag ID numbers

3.2.9 Condition of the shipping container

3.2.10 Condition of the sample bottles

3.2.11 Verification of agreement or non-agreement of information on receiving documents and sample containers

3.2.12 Resolution of problems or discrepancies with the SMO

3.2.13 An explanation of any terms used by the laboratory to describe sample condition upon receipt (e.g., good, fine, OK)

3.3 The Contractor shall have written SOPs for maintaining identification of EPA samples throughout the laboratory.

If the Contractor assigns unique laboratory identifiers, written SOPs shall include a description of the method used to assign the unique laboratory identifier and shall include a description of the document used to cross-reference the unique laboratory identifier to the EPA sample number.

If the Contractor uses prefixes or suffixes in addition to sample identification numbers, the written SOPs shall include their definitions.

3.4 The Contractor shall have written SOPs describing all storage areas for samples in the laboratory. The SOPs shall include a list of authorized personnel who have access or keys to secure storage areas.

3.5 The Contractor shall have written SOPs describing the method by which the laboratory maintains samples under custody.

3.6 The Contractor shall have written SOPs describing the method by which the laboratory maintains the security of any areas identified as secure.

3.7 The Contractor shall have written SOPs for tracking the work performed on any particular samples. The tracking SOP shall include:

- o A description of the documents used to record sample receipt, sample storage, sample transfers, sample preparations, and sample analyses.
- o A description of the documents used to record calibration and QA/QC laboratory work.
- o Examples of document formats and laboratory documents used in the sample receipt, sample storage, sample transfer, and sample analyses.
- o A narrative step-wise description of how documents are used to track samples.

3.8 The Contractor shall have written SOPs for organization and assembly of all documents relating to each SDG. Documents shall be filed on a sample delivery group-specific basis. The procedures shall ensure that all documents including logbook pages, sample tracking records, chromatographic charts, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the SDG are compiled in one location for submission to EPA. The written SOPs shall include:

- o A description of the numbering and inventory method.
- o A description of the method used by the laboratory to verify consistency and completeness of the CSF.
- o Procedures for the shipment of deliverables packages using custody seals.

4. HANDLING OF CONFIDENTIAL INFORMATION

A Contractor conducting work under this contract may receive EPA-designated confidential information from the agency. Confidential information must be handled separately from other documentation developed under this contract. To accomplish this, the following procedures for the handling of confidential information have been established.

4.1 All confidential documents shall be under the supervision of a designated Document Control Officer (DCO).

4.2 Confidential Information

Any samples or information received with a request of confidentiality shall be handled as "confidential." A separate locked file shall be maintained to store this information and shall be segregated from other nonconfidential information. Data generated from confidential samples shall be treated as confidential. Upon receipt of confidential information, the DCO will log these documents into a Confidential Inventory Log. The information will then be available to authorized personnel but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by the EPA Administrative or Technical Project Officer. The DCO will enter all copies into the document control system described above. In addition, this information may not be disposed of except upon approval by the EPA Administrative or Technical Project Officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record on the disposition in the Confidential Inventory Log.

EXHIBIT G

GLOSSARY OF TERMS

GLOSSARY OF TERMS

ABSORBANCE - a measure of the decrease in incident light passing through a sample into the detector. It is defined mathematically as:

$$A = \frac{I(solvent)}{I(solution)} = \log \frac{Io}{I}$$

Where, I = radiation intensity

ALIQUOT - a measured portion of a field sample taken for analysis.

ANALYSIS DATE/TIME - the date and military time (24-hour clock) of the introduction of the sample, standard, or blank into the analysis system.

ANALYTE - the element or ion an analysis seeks to determine; the element of interest.

ANALYTICAL SAMPLE - Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification and continuing calibration blank. Note the following are all defined as analytical samples: undiluted and diluted samples (EPA and non-EPA), predigestion spike samples, duplicate samples, serial dilution samples, analytical spike samples, post-digestion spike samples, interference check samples (ICS), CRDL standard for AA (CRA), CRDL standard for ICP (CRI), laboratory control sample (LCS), preparation blank (PB) and linear range analysis sample (LRS).

ANALYTICAL SPIKE - The furnace post-digestion spike. The addition of a known amount of standard after digestion.

AUTOZERO - zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

AVERAGE INTENSITY - The average of two different injections (exposures).

BACKGROUND CORRECTION - a technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

BATCH - a group of samples prepared at the same time in the same location using the same method.

CALIBRATION - the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation.

CALIBRATION BLANK - a volume of acidified deionized/distilled water.

CALIBRATION STANDARDS - a series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

CASE - a finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office. A Case consists of one or more Sample Delivery Groups.

COEFFICIENT OF VARIATION (CV) - the standard deviation as a percent of the arithmetic mean.

CONCENTRATION LEVEL (low or medium) - for inorganics analysis, low or medium level is defined by the appropriate designation checked by the sampler on the Traffic Report.

CONTINUING CALIBRATION - analytical standard run every 10 analytical samples or every 2 hours, whichever is more frequent, to verify the calibration of the analytical system.

CONTRACT REQUIRED DETECTION LIMIT (CRDL) - minimum level of detection acceptable under the contract Statement of Work.

CONTROL LIMITS - a range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

CORRELATION COEFFICIENT - a number (r) which indicates the degree of dependence between two variables (concentration - absorbance). The more dependent they are the closer the value to one. Determined on the basis of the least squares line.

DAY - unless otherwise specified, day shall mean calendar day.

DIGESTION LOG - an official record of the sample preparation (digestion).

DISSOLVED METALS - analyte elements which have <u>not</u> been digested prior to analysis and which will pass through a 0.45 um filter.

DRY WEIGHT - the weight of a sample based on percent solids. The weight after drying in an oven.

DUPLICATE - a second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

FIELD BLANK - any sample submitted from the field identified as a blank.

FIELD SAMPLE - a portion of material received to be analyzed that is contained in single or multiple containers and identified by a unique EPA Sample Number.

FLAME ATOMIC ABSORPTION (AA) - atomic absorption which utilizes flame for excitation.

GRAPHITE FURNACE ATOMIC ABSORPTION (GFAA) - atomic absorption which utilizes a graphite cell for excitation.

HOLDING TIME - the elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

Holding time = (sample analysis date - sample receipt date)

INDEPENDENT STANDARD - a Contractor-prepared standard solution that is composed of analytes from a different source than those used in the standards for the initial calibration.

INDUCTIVELY COUPLED PLASMA (ICP) - a technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency inductively coupled plasma.

IN-HOUSE - at the Contractor's facility.

INJECTION - introduction of the analytical sample into the instrument excitation system for the purpose of measuring absorbance, emission or concentration of an analyte. May also be referred to as exposure.

INSTRUMENT CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

INSTRUMENT DETECTION LIMIT (IDL) - determined by multiplying by three the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3x-5x IDL on three nonconsecutive days with seven consecutive measurements per day.

INSTRUMENT CHECK SAMPLE - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

INSTRUMENT CHECK STANDARD - a multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis.

INTERFERENTS - substances which affect the analysis for the element of interest.

INTERNAL STANDARDS - in-house compounds added at a known concentration.

LABORATORY - synonymous with Contractor as used herein.

LABORATORY CONTROL SAMPLE (LCS) - a control sample of known composition. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents, and analytical methods employed for the EPA samples received.

LABORATORY RECEIPT DATE - the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Traffic Report. Also referred to as VTSR (validated time of sample receipt).

LINEAR RANGE, LINEAR DYNAMIC RANGE - the concentration range over which the ICP analytical curve remains linear.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX MODIFIER - salts used in AA to lessen the effects of chemical interferents, viscosity, and surface tension.

MATRIX SPIKE - aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

METHOD OF STANDARD ADDITIONS (MSA) - the addition of 3 increments of a standard solution (spikes) to sample aliquots of the same size. Measurements are made on the original and after each addition. The slope, x-intercept and y-intercept are determined by least-square analysis. The analyte concentration is determined by the absolute value of the x-intercept. Ideally, the spike volume is low relative to the sample volume (approximately 10% of the volume). Standard addition may counteract matrix effects; it will not counteract spectral effects. Also referred to as Standard Addition.

PERCENT SOLIDS - the proportion of solid in a soil sample determined by drying an aliquot of the sample.

PERFORMANCE EVALUATION (PE) SAMPLE - a sample of known composition provided by EPA for Contractor analysis. Used by EPA to evaluate Contractor performance.

PREPARATION BLANK (reagent blank, method blank) - an analytical control that contains distilled, deionized water and reagents, which is carried through the entire analytical procedure (digested and analyzed). An aqueous method blank is treated with the same reagents as a sample with a water matrix; A solid method blank is treated with the same reagents as a soil sample.

PROTOCOL - a compilation of the procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Used synonymously with Statement of Work (SOW).

QUALITY CONTROL SAMPLE - a solution obtained from an outside source having known concentration values to be used to verify the calibration standards.

REAGENT BLANK - a volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme.

ROUNDING RULES - If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

See forms instructions (Exhibit B) for exceptions.

RUN - a continuous analytical sequence consisting of prepared samples and all associated quality assurance measurements as required by the contract Statement of Work.

SAMPLE DELIVERY GROUP (SDG) - a unit within a sample Case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer samples within a Case, received over a period of up to 14 calendar days. Data from all samples in an SDG are due concurrently. A Sample Delivery Group is defined by one of the following, whichever occurs first:

- Case; or
- Each 20 samples within a Case; or
- Each 14-day calendar period during which samples in a Case are received, beginning with receipt of the first sample in the Case or SDG.

Samples may be assigned to Sample Delivery Groups by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory.

SAMPLE NUMBER (EPA SAMPLE NUMBER) - a unique identification number designated by EPA for each sample. The EPA Sample Number appears on the sample Traffic Report which documents information on that sample.

SENSITIVITY - the slope of the analytical curve, i.e., functional relationship between emission intensity and concentration.

SERIAL DILUTION - the dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

SOIL - synonymous with soil/sediment or sediment as used herein.

STOCK SOLUTION - a standard solution which can be diluted to derive other standards.

SUSPENDED - those elements which are retained by a 0.45 um membrane filter.

TOTAL METALS - analyte elements which have been digested prior to analysis.

TRAFFIC REPORT (TR) - an EPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and which is used for documenting sample condition and receipt by the laboratory.

WET WEIGHT - the weight of a sample aliquot including moisture (undried).

10% FREQUENCY - a frequency specification during an analytical sequence allowing for no more than 10 analytical samples between required calibration verification measurements, as specified by the contract Statement of Work.

EXHIBIT H

DATA DICTIONARY AND FORMAT FOR DATA
DELIVERABLES IN COMPUTER-READABLE FORMAT

AGENCY STANDARD IMPLEMENTATION FOR INORGANICS ILM02.1

1. Format Characteristics

1.1 This constitutes an implementation of the EPA Agency Standard for Electronic Data Transmission based upon analytical results and ancillary information required by the contract. All data generated by a single analysis are grouped together, and the groups are aggregated to produce files that report data from an SDG. Because this implementation is only a subset of the Agency Standard, some fields have been replaced by delimiters as place holders for non-CLP data elements.

1.2 This implementation includes detailed specifications for the required format of each record. The position in the record where each field is to be contained relevant to other fields is specified, as well as the maximum length of the field. Each field's required contents are specified as literal (contained in quotes), which must appear exactly as shown (without quotes), or as a variable for which format and/or descriptions are listed in the format/contents column. Options and examples are listed for most fields. For fields where more than three options are available, a list and description of options are supplied following the record descriptions. Fields are separated from each other by the delimiter "|" (ASCII 124). Fields that do not contain data should be zero length with the delimiter as place holder.

1.3 Numeric fields may contain numeric digits, a decimal place, and a leading minus sign. A positive sign is assumed if no negative sign is entered in a numeric field and must not be entered into any numeric field.

Requirements for significant figures and number of decimal places are specified in Exhibit B. The numeric field lengths are specified such that all possible numeric values can be written to the file. The size of the numeric field indicates the maximum number of digits, decimal, and negative sign, if appropriate, that can appear in the field at the same time. Therefore, the number reported may need to be rounded (using EPA Rounding Rules) to fit into the field. The rounding must maintain the greatest significance possible providing the field length limitation. In addition, the rounded number that appears on the form, and therefore the field in the diskette file, must be used in any calculation that may result in other numbers reported on the same form or other forms in the SDG. Field lengths should only be as long as necessary to contain the data; packing with blanks is not allowed.

2. Record Types

2.1 The Agency Standard consists of variable length ASCII records. Maximum field length specifications match the reporting requirements in Exhibit B. The last two bytes of each record must contain "carriage return" and "line feed", respectively.

2.2 There are four groups of record types in the reporting format, as shown below. Detailed record formats follow.

Type	Type ID	Contents
Run Header	10	Information pertinent to a group of samples processed in a continuous sequence; usually several per SDG
Sample Header	20	Sample identifying, qualifying, and linking information
Results Record	30	Analyte results and qualifications
Comments Record	90	Free form comments

2.3 All record types given are mandatory. Type 10, representing the analytical run, contains the instrument and run IDs which act as an identifying label for the run. All 10, 20, 30, and 90 series records following that record pertain to the same analytical run. Type 20, representing the sample, contains the EPA Sample ID which acts as an identifying label for the sample. The QC code indicates whether the data is from an environmental sample, calibration, or QC sample. All 20, 30, and 90 series records following that record pertain to the same sample. Type 30, representing an individual analyte, contains an identifier to identify the analyte. All 30 series records following that record pertain to the same analyte.

3. Production Runs

A production run represents a "group" or "batch" of samples that are processed in a continuous sequence under relatively stable conditions. Specifically:

Calibration - All samples in a run use the same initial calibration data.

Method - Constant.

Instrument conditions - Constant throughout a run. Results obtained on different instruments cannot be combined in one run.

Thus, each separate group of analyses on each instrument will consist of a separate production run, and must be reported in a separate file.

Example of the Sequence of Record Types in a Production Run

10 Contains run header information. Occurs once per run.

16 Contains additional run header information. Occurs once per run.

20 Acts as a header for the following instrument parameter information. Occurs once per run with EPA Sample Number equal to "IDL". Analysis year, analysis month, analysis day equal the year, month and day the IDLs were computed. Analyte count equals the number of the type 30 records that follow.

30 Contains only the Analyte CAS Number, IDL Label and IDL. Occurs once for each analyte used in the run.

30

30

30

20 Acts as a header for the following instrument parameter information. Occurs once per run with EPA Sample Number equal to "LRV". Analysis year, analysis month, analysis day equal to the year, month and day the linear ranges were computed. Analyte count equals the number of type 30, 32 and 34 groups that follow.

30 Contains only the Analyte CAS Number. Occurs once for each analyte used in the run.

32 Contains integration time information for the preceding analyte on the type 30 record.

34 Contains the CRDL and Linear Range information for the preceding analyte on the type 30 record. There are as many consecutive type 34 records as there are different wavelengths used for the analyte identified on preceding type 30.

30

32

34

20 Acts as a header for the following instrument parameter information. Occurs once per run with EPA Sample Number equal to "ICF". Analysis year, analysis month, analysis day equal the year, month and day the interelement correction factors were computed. Analyte count equals the number of the type 30 and 35 groups that follow.

30 Contains only the Analyte CAS Number. Occurs once for each analyte used in the run.

35 Contains the background and interelement correction information for the preceding analyte on the type 30 record. There are as many consecutive type 35 records as there are interelement correction factors for the analyte identified on preceding type 30.

30

35

20 Contains header information for sample and QC data.

21 Contains additional information for analytical and instrument QC samples. Will always be preceded by a type 20 record.

22 Contains additional information for analytical samples. Will usually follow type 21 record.

30 Contains the sample level concentration, true or added value and QC value for each analyte. Occurs once for each analytical result for the EPA Sample Number of the previous type 20 record.

31 Reports any instrumental data necessary to obtain the result reported on the previous type 30 record. Will always be preceded by a type 30 record. Occurs once per type 30 record.

30 Values for the next analyte wavelength being measured.

31 Values for the next analyte wavelength being measured.

30

31

Type 30-31 record sequence continues as many times as the value of the ANALYTE COUNT on the previous type 20 record.

20 Next Sample Header record - The following applies to the next sample data.

21

22

30

31

30

31 etc.

20

21

22

30

31

etc.

4. Record Sequence

4.1 A Run Header (type 10) record must be present as the first record in the file. Further occurrences of the type 10 record in the file are not allowed.

A type 16 record must immediately follow the type 10 record. Further occurrences of the type 16 record in the file are not allowed.

The first three type 20 records are headers for the calculated run-wide instrument parameters. The first type 20 record is a header for the quarterly determined instrument detection limit values (IDL) and must immediately follow the type 16 record. The second type 20 record is a header for the linear range values (LRV) and must immediately follow the last type 30 record that pertains to the instrument detection limit values. The third type 20 record is a header for the annually determined ICP interelement correction factors (ICF) and must immediately follow the last type 34 record that pertains to the linear range values. These are the only occurrences of the type 20 records that do not correspond to actual analyses in the run. Therefore, the only fields that are not blank in these occurrences of the type 20 record are the RECORD TYPE ("20"); EPA SAMPLE NUMBER ("IDL", "LRV" and "ICF"); Analysis Year/Year Computed, Analysis Month/Month Computed, Analysis Day/Day Computed ("YY", "MM", "DD"); and ANALYTE COUNT.

A minimum of one type 30 record must immediately follow the first type 20 record, and the total number of type 30 records must be equivalent to the ANALYTE COUNT on this type 20 record. A minimum of one group of type 30, 32 and 34 records must immediately follow the second type 20 record. The information in each group must pertain to one and only one analyte. The number of groups must be equivalent to the Analyte Count on the second type 20 record. A minimum of one group of type 30 and 35 records must immediately follow the third type 20 record. The information in each group must pertain to one and only one analyte. The number of groups must be equivalent to the analyte count on the third type 20 record. This last group must immediately be followed by the first type 20 record that corresponds to an actual analysis of an instrument calibration standard. After the appearance of this, the fourth type 20 record in the file, further occurrences of the type 32, 34 and 35 records in that file are not allowed.

4.2 Each environmental sample, calibration, or quality control sample is represented by a group composed of a type 20, 21, and 22 records, which holds sample level identifying information, followed by a minimum of one group composed of type 30 and 31 records for each analyte's wavelength.

The type 20 record holds a count for the number of analyte wavelengths being used to determine results. The ANALYTE COUNTER must have a value equivalent to the number of type 30 groups associated with each type 20 record.

Except for the first three type 20 records, all type 20 records should occur in the order of sample analysis.

4.3 Type 90 comment records may be defined to occupy any position except before the type 10 (header) record. Comments pertaining to the whole run such as ones on Cover Page must appear before the first type 20 record. Comments pertaining to a particular sample such as ones on Form I must appear after the type 20 record for that sample, but before the first type 30 record associated with that sample. Comments pertaining to a particular analyte or wavelength must appear after the type 30 record of that wavelength, but before the type 30 record of the following wavelength.

5. File/Record Integrity

All record types must contain the following check fields to ensure file and record integrity:

Record Position	Field Length	Contents	Remarks
First Field	2	Record type or identifier	"10" or as appropriate
Last Field	5	Record sequence number within file	00000-99999, repeated as necessary
	4	Record checksum	Four hexadecimal digits*
	2	Contains CR and LF	

* The checksum is defined to be the sum of the ASCII representation of the data on the record up to the Record Sequence Number plus the checksum of the previous record. The sum is taken modulo 65536 (2^{16}) and represented as four (4) hexadecimal digits.

6. Dates and Times

Date or time-of-day information consists of successive groups of two decimal digits, each separated by delimiters. Dates are given in the order YY MM DD, and times as HH MM. All hours must be given as 00 to 23 using a 24 hour clock and must be local time.

7. Multiple Volume Data

There is no requirement under this format that all the data from an entire SDG fit onto a single diskette. However, each single production run must fit onto a single diskette if possible. If that is not possible, then it is necessary that all files start with a type 10 record, and that the multiple type 10 records for each file of the same production run be identical. Information for a single sample may not be split between files.

8. Deliverable

8.1 The file or files must be submitted on a 5-1/4 inch floppy diskette, which may be either a double-sided, double-density, 360 K-byte or a high capacity 1.2 M-byte, or 3.5 inch double-sided, double-density 720 K-byte or 1.44 M-byte, diskette. The diskette must be formatted and recorded using the MS-DOS Operating System. The diskette or diskettes must contain all information relevant to one and only one SDG, and must accompany the hardcopy package for the SDG submitted to the Sample Management Office (see Exhibit B). Information on the diskette or diskettes must correspond exactly with information submitted in the hardcopy data package and on the hardcopy data package forms. Blank or unused records should not be included on the diskettes.

8.2 Each diskette must be identified with an external label containing (in this order) the following information:

Disk Density
File Name(s)
Laboratory Name (optional)
Laboratory Code
Case Number (where applicable)
SAS Number (where applicable)

The format for the File Name(s) must be XXXXXX.I01 to XXXXXX.I99

where XXXXXX is the SDG identifier, I designates inorganics, and 01 through 99 the file number.

Dimensions of the label must be in the range 4-3/4" to 5" long by 1 1/4" to 1 1/2" wide for 5 1/4 inch floppy diskette; and 2" to 2 1/4" long by 2 1/8" to 2 3/8" wide for 3.5 inch IBM-compatible diskette.

9. Record Listing

Following is a listing of every record type required to report data from a single SDG.

FORMAT OF THE PRODUCTION RUN FIRST HEADER RECORD (TYPE 10)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"10"
1	Delimiter	|
2	ANALYSIS START YEAR	YY
1	Delimiter	|
2	ANALYSIS START MONTH	MM
1	Delimiter	|
2	ANALYSIS START DAY	DD
1	Delimiter	|
2	ANALYSIS START HOUR	HH
1	Delimiter	|
2	ANALYSIS START MINUTE	MM
1	Delimiter	|
5	METHOD TYPE	CHARACTER[1]
1	Delimiter	|
8	METHOD NUMBER	"ILM02.1" (SOW)
1	Delimiter	|
3	MANAGER'S INITIALS	CHARACTER
1	Delimiter	|
6	LAB CODE	CHARACTER
4	Delimiter	||||
11	CONTRACT NUMBER	CHARACTER
1	Delimiter	|
10	INSTRUMENT ID	CHARACTER
2	Delimiter	||
25	LABORATORY NAME	CHARACTER
1	Delimiter	|
2	RUN NUMBER	NUMERIC[2]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

---

1 Method Types are
"P" for ICP
"A" for Flame AA
"F" for Furnace AA
"PM" for ICP when Microwave Digestion is used
"AM" for Flame AA when Microwave Digestion is used
"FM" for Furnace AA when Microwave Digestion is used
"CV" for Manual Cold Vapor AA
"AV" for Automated Cold Vapor AA
"CA" for Midi-Distillation Spectrophotometric
"AS" for Semi-Automated Spectrophotometric
"C" for Manual Spectrophotometric
"T" for Titrimetric

2 Run number values are 01 through 99. Each production run will be assigned a unique Run Number. Run Numbers are to be assigned sequentially beginning with 01 and will equal the number of production runs.

FORMAT OF THE PRODUCTION RUN SECOND HEADER RECORD (TYPE 16)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"16"
1	Delimiter	|
2	ANALYSIS END YEAR	YY
1	Delimiter	|
2	ANALYSIS END MONTH	MM
1	Delimiter	|
2	ANALYSIS END DAY	DD
1	Delimiter	|
2	ANALYSIS END HOUR	HH
1	Delimiter	|
2	ANALYSIS END MINUTE	MM
1	Delimiter	|
1	AUTO-SAMPLER USED	"Y" or "N"[1]
1	Delimiter	|
1	INTERELEMENT CORRECTIONS APPLIED	"Y" or "N"[2]
1	Delimiter	|
1	BACKGROUND CORRECTIONS APPLIED	"Y" or "N"[2]
1	Delimiter	|
1	RAW DATA GENERATED	"Y" or "N" or "B"[3]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

---

1 Enter "Y" if an auto-sampler is used with equal analysis time and intervals between analysis.

2 These are the answers to the first two questions on the Cover Page. "Y" equals "YES", and "N" equals "NO".

3 This is the answer to the third question on the Cover Page. "Y" equals "YES", "B" equals BLANK and "N" equals "NO".

FORMAT FOR THE MANDATORY SAMPLE HEADER DATA RECORD (TYPE 20)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"20"
1	Delimiter	|
2	REGION	NUMERIC
1	Delimiter	|
12	EPA SAMPLE NUMBER	CHARACTER[1]
1	Delimiter	|
5	MATRIX	CHARACTER[2]
1	Delimiter	|
3	*QC CODE*	CHARACTER
1	Delimiter	|
3	SAMPLE QUALIFIER	CHARACTER[3]
1	Delimiter	|
5	CASE NUMBER	CHARACTER
1	Delimiter	|
6	SDG NUMBER	CHARACTER
1	Delimiter	|
2	ANALYSIS YEAR/YEAR COMPUTED	YY
1	Delimiter	|
2	ANALYSIS MONTH/MONTH COMPUTED	MM
1	Delimiter	|
2	ANALYSIS DAY/DAY COMPUTED	DD
1	Delimiter	|
2	ANALYSIS HOUR	HH
1	Delimiter	|
2	ANALYSIS MINUTE	MM
2	Delimiter	||
2	SAMPLE WT/VOL UNITS	"G"/"ML"[4]
1	Delimiter	|
5	SAMPLE WT/VOL	NUMERIC[5]
1	Delimiter	|
3	ANALYTE COUNT	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

---

1 EPA Sample Number as appears on Form XIV except for the first three type 20 records. The first type 20 record must have an EPA Sample Number of "IDL"; the second, an EPA sample number of "LRV"; the third, an EPA sample number of "ICF".

2 For matrix, "1" equals "WATER", and "F" equals "SOIL".

3 "REJ" sample qualifier is for the unacceptable (one of the two) MSA results; this sample qualifier appears on the type 20 record containing the zero (0) addition EPA Sample Number (XXXXXX0).

4 "G" equals grams, and "ML" equals milliliters.

5 This is the size of the sample at the beginning of the digestion procedure.

SAMPLE QC CODES LISTING FOR TYPE 20

QCC	Name	Definition
LRB	LABORATORY (REAGENT) BLANK	The Preparation or Method Blank (See Exhibit G).
LCB	LABORATORY CALIBRATION BLANK	The Continuing Calibration Blank (CCB) (See Exhibit G).
LIB	LABORATORY INITIAL BLANK	The Initial Calibration Blank (ICB) (See Exhibit G).
LCM	LABORATORY CONTROL SOLUTION	The Laboratory Control Sample (LCS) (See Exhibit G).
LD1	LABORATORY DUPLICATE FIRST MEMBER	This is the same as the Sample Result "(S)" that is reported on the Duplicate Form of hardcopy (Form VI).
LD2	LABORATORY DUPLICATE SECOND MEMBER	This is the second aliquot and is identified as "D" on the Duplicate Form of hardcopy (Form VI).
LVM	LABORATORY CALIBRATION VERIFICATION SOLUTION	These values are identified as "Initial Calibration Verification" (ICV) on Form II (Part 1).
LVC	LABORATORY CONTINUING CALIBRATION VERIFICATION	These values are identified as "Continuing Calibration Verification" (CCV) on Form II (Part 1).
LSO	LABORATORY SPIKED SAMPLE BACKGROUND (ORIGINAL) VALUES	These values are identified as "Sample Result (SR)" on the "Spike Sample Recovery" Form of hardcopy (Form V (Part 1)).
LSF	LABORATORY SPIKED SAMPLE-FINAL VALUES	These are the "Spiked Sample Result (SSR)" values on the "Spike Sample Recovery" Form of hardcopy (Form V (Part 1)).
LDO	LABORATORY DILUTED SAMPLE BACKGROUND (ORIGINAL) VALUES	These values are the "Initial Sample Result (I)" values on the "Serial Dilution" Form of hardcopy (Form IX).
LDF	LABORATORY DILUTED SAMPLE - FINAL VALUES	These are the "Serial Dilution Result(S)" values on the "Serial Dilution" Form of hardcopy (Form IX).

SAMPLE QC CODES LISTING FOR TYPE 20

QCC	Name	Definition
MS0	STANDARD ADDITION RESULTS ORIGINAL VALUE	This value is identified as "0 ADD" on "Standard Addition Results", Form VIII.
MS1	STANDARD ADDITION RESULTS FIRST ADDITION	This value is identified as "1 ADD" on "Standard Addition Results", Form VIII.
MS2	STANDARD ADDITION RESULTS SECOND ADDITION	This value is identified as "2 ADD" on "Standard Addition Results", Form VIII.
MS3	STANDARD ADDITION RESULTS THIRD ADDITION	This value is identified as "3 ADD" on "Standard Addition Results", Form VIII.
PDO	POST DIGESTION SPIKE BACKGROUND (ORIGINAL) VALUES	This value is identified as "Sample Result" (SR) on the "Post Digest Spike Sample Recovery", Form V (Part 2), or GFAA original sample analysis.
PDF	POST DIGESTION SPIKE BACKGROUND (FINAL) VALUES	This value is identified as "Spiked Sample Result" (SSR) on the "Post Digest Spike Sample Recovery", Form V (Part 2), or GFAA post digestion spiked sample analysis.
LPC	CRDL STANDARD	Laboratory Performance Check Solution for ICP (CRI) and Graphite Furnace (CRA).
LII	LABORATORY INTERFERENCE CHECK SOLUTION (INITIAL)	The results of this solution analysis are reported on the "Interference Check Sample" (ICS), Form IV.
LIF	LABORATORY INTERFERENCE CHECK SOLUTION (FINAL)	The results of this solution analysis are reported on the "Interference Check Sample" (ICS), Form IV.

FORMAT OF THE SAMPLE HEADER RECORD (TYPE 21)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"21"
2	Delimiter	||
3	LEVEL	"LOW"/"MED"
3	Delimiter	|||
6	SAS NUMBER	CHARACTER
1	Delimiter	|
14	LAB SAMPLE ID	CHARACTER
1	Delimiter	|
2	PREPARATION YEAR	YY
1	Delimiter	|
2	PREPARATION MONTH	MM
1	Delimiter	|
2	PREPARATION DAY	DD
2	Delimiter	||
2	YEAR RECEIVED	YY
1	Delimiter	|
2	MONTH RECEIVED	MM
1	Delimiter	|
2	DAY RECEIVED	DD
1	Delimiter	|
9	COMPOUND SOURCE	CHARACTER
1	Delimiter	|
8	INJECTION/ALIQUOT VOLUME	NUMERIC[1]
1	Delimiter	|
2	PREPARATION START HOUR	HH[2]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

---

1 This is the portion of the sample that is injected into the instrument excitation system for the purpose of measuring the absorbance, emission or concentration of an analyte.

2 This is the hour at which the preparation is started. It is used to differentiate between different batches on the same day.

FORMAT OF THE ASSOCIATED INJECTION AND COUNTER RECORD (TYPE 22)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"22"
10	Delimiter	||||||||||
8	EXTRACT VOLUME	NUMERIC[1]
1	Delimiter	|
8	DILUTION FACTOR	NUMERIC
3	Delimiter	|||
5	PERCENT SOLIDS	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

[1] This is the final volume of the digestion procedure that is currently reported on Form XIII of the hardcopy.

FORMAT OF THE RESULTS DATA RECORD (TYPE 30)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"30"
1	Delimiter	|
1	ANALYTE IDENTIFIER	"C"/"I"[1]
1	Delimiter	|
9	ANALYTE CAS NUMBER	CHARACTER
2	Delimiter	||
5	CONCENTRATION UNITS	"UG/L"/"MG/KG"
1	Delimiter	|
3	CONCENTRATION QUALIFIER	CHARACTER[2]
1	Delimiter	|
10	CONCENTRATION	NUMERIC
1	Delimiter	|
1	VALUE DESCRIPTOR	"T/"F"[3]
1	Delimiter	|
10	AMOUNT ADDED OR TRUE VALUE	NUMERIC
1	Delimiter	|
1	QC VALUE DESCRIPTOR	"P"/"C"/"L"[4]
1	Delimiter	|
10	QC VALUE	NUMERIC
1	Delimiter	|
2	QC LIMIT QUALIFIER	"N"/"*"/"+"/"E"[5]
1	Delimiter	|
10	QC LOWER LIMIT	NUMERIC
1	Delimiter	|
10	QC UPPER LIMIT	NUMERIC
1	Delimiter	|
1	IDL LABEL	"U" for undetected
1	Delimiter	|
10	IDL	NUMERIC[6]
1	Delimiter	|
1	RAW DATA AVERAGE QUALIFIER	"U"/"B"/"L"[7]
1	Delimiter	|
10	RAW DATA AVERAGE	NUMERIC
1	Delimiter	|
1	RAW DATA %RSD QUALIFIER	"M"/BLANK
1	Delimiter	|
10	RAW DATA %RSD	NUMERIC
1	Delimiter	|
1	RAW DATA "MSA-TREE" QUALIFIER	"E"/"W"/BLANK
1	Delimiter	|
10	RAW DATA ANALYTICAL SPIKE %R	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NO.	NUMERIC
4	CHECKSUM	CHARACTER

FORMAT OF THE RESULTS DATA RECORD (TYPE 30) FOOTNOTES

1 "C" (CAS Registry Number) is used for all analytes except cyanide. "I" is used for cyanide.

2 "BDL" means below detection limit.

"NSQ" means there is not sufficient quantity to analyze sample according to the protocol.

"NAI" not analyzed due to interference, "NAR" no analysis result required.

Note that there is no absolute equivalent to the final concentration on Form VIII in Standard EPA Format.

"LTC" means less than the CRDL but greater than or equal to the IDL.
"FQC" means failed quality control criteria.

"GTL" means greater than the linear range.

"RIN" means that the analysis result were not used to report data in the SDG. The results are reported from a later reanalysis of the same sample aliquot.

"REX" means that the analysis result were not used to report data in the SDG. The results are reported from a later reanalysis of a repreparation of same sample.

Note that, except for "NAR", none of these codes the Contractor from reporting a valid result. They only explain why or if the result is qualified.

3 "T" stands for a true value of the solution. This includes the concentration of all (ICP as well) instrument calibration standards. "F" stands for an added concentration to a sample such as a pre or post digestion spike, or MSA additions.

4 "P" equals percent, "C" equals correlation coefficient, and "L" equals control limit.

5 "N" equals spiked sample recovery not within control limits, "*" equals duplicate analysis not within control limits, "+" equals correlation coefficient for the MSA less than 0.995, "E" equals the estimated reported value because of the presence of interference. "S" flag is not applicable for Standard EPA Format.

6 The IDL must be a whole number for all analytes except for mercury. Mercury must be reported to one decimal place.

7 "U" means less than the IDL, "B" means less than the CRDL and greater than or equal to the IDL, "L" means greater than the linear range.

FORMAT FOR THE INSTRUMENTAL DATA READOUT (TYPE 31)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"31"
1	Delimiter	|
1	TYPE OF DATA	"W"[1]
1	Delimiter	|
1	TYPE OF VALUE	CHARACTER[2]
2	Delimiter	||
8	ANALYTE WAVELENGTH	NUMERIC (TO 2 DECIMAL PLACES)
1	Delimiter	|
10	FIRST INSTRUMENT VALUE	NUMERIC[3,4]
2	Delimiter	||
10	SECOND INSTRUMENT VALUE	NUMERIC[3]
2	Delimiter	||
10	THIRD INSTRUMENT VALUE	NUMERIC[3]
2	Delimiter	||
10	FOURTH INSTRUMENT VALUE	NUMERIC[3]
2	Delimiter	||
10	FIFTH INSTRUMENT VALUE	NUMERIC[3]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

---

1 "W" equals wavelength.

2 "C" equals concentration in ug/L, "T" equals concentration in ug/250 ml, "F" equals concentration in ug/50 ml, "B" equals absorbance, "I" equals intensity, "A" equals peak area in cm square, and "H" equals peak height in cm.

3 This is used to report data for method analyses that require replicate injections or exposures. If a single instrument measurement is used, then enter it in the first instrument value field, and leave the other four fields empty. If two instrument measurements are used, then enter them in the first and second instrument value fields in the order of their analyses, and leave the other three fields empty; etc.

4 For MSA, the absorbances for the zero, first, second and third additions with EPA Sample Numbers XXXXXX0, XXXXXX1, XXXXXX2, XXXXXX3 are reported in this, the first instrument value, field; and the final concentration obtained from the MSA is entered in the "concentration" field on the type 30 record which corresponds to the type 20 record that contains the EPA Sample Number XXXXXX0.

FORMAT OF THE AUXILLIARY DATA RECORD (TYPE 32)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"32"
10	Delimiter	||||||||||
2	INTEGRATION TIME CODE	"IT"
1	Delimiter	|
10	INTEGRATION TIME	IN SECONDS
4	Delimiter	||||
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

FORMAT OF THE QC LIMIT RECORD (TYPE 34)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"34"
4	Delimiter	||||
8	ANALYTE WAVELENGTH	NUMERIC (TO 2 DECIMAL PLACES)
1	Delimiter	|
10	CRDL	NUMERIC
1	Delimiter	|
10	LINEAR RANGE	NUMERIC
6	Delimiter	||||||
5	RECORD SEQUENCE NO.	NUMERIC
4	CHECKSUM	CHARACTER

FORMAT OF THE CORRECTION DATA RECORD (TYPE 35)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"35"
1	Delimiter	|
3	TYPE OF CORRECTION	"ICP"/"BG"[1]
1	Delimiter	|
5	TYPE OF BACKGROUND	"BS"/"BD"/"BZ"
4	Delimiter	||||
9	INTERFERING ANALYTE	CHARACTER
1	Delimiter	|
8	ANALYTE WAVELENGTH	NUMERIC (TO 2 DECIMAL PLACES)
1	Delimiter	|
10	CORRECTION FACTOR	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NO.	NUMERIC
4	CHECKSUM	CHARACTER

1 "ICP" indicates interelement correction, while "BG" indicates a background correction.

FORMAT OF THE COMMENT RECORD (TYPE 90)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"90"
1	Delimiter	|
67	ANY COMMENT	CHARACTER
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

FORMAT OF THE SAMPLE ASSOCIATED DATA RECORD (TYPE 92)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"92"
1	Delimiter	|
9	COLOR BEFORE	CHARACTER
1	Delimiter	|
9	COLOR AFTER	CHARACTER
1	Delimiter	|
6	CLARITY BEFORE	CHARACTER
1	Delimiter	|
6	CLARITY AFTER	CHARACTER
1	Delimiter	|
6	TEXTURE	CHARACTER
1	Delimiter	|
3	ARTIFACTS	"YES"/BLANK
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER