United States
Environmental Protection
Agency

Office of
Solid Waste and
Emergency Response

Publication 9240.1-11
EPA/540/R/94/074
PB95-963504
December 1994

Superfund

EPA

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK FOR INORGANIC ANALYSIS MULTI-MEDIA, HIGH-CONCENTRATION

IHCO 1.3

9240.1-11
PB95-963504
EPA540/R-94/074

Attachment A

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR

INORGANIC ANALYSIS

Multi-Media

High-Concentration

(HCIN)

Document Number IHC01.3

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590

STATEMENT OF WORK

TABLE OF CONTENTS

			Page
PREFACE:			i
EXHIBIT A:	SUMMARY OF REQUIREMENTS		1
	I.	Summary of Method	3
	II.	General Requirements	5
	III.	Specific Requirements	7
EXHIBIT B:	REPORTING AND DELIVERABLES REQUIREMENTS		13
	I.	Contract Reports/Deliverables Distribution	15
	II.	Report Descriptions and Order of Data Deliverables	17
	III.	Form Instruction Guide	27
	IV.	Data Reporting Forms	55
EXHIBIT C:	INORGANIC ANALYTE TABLES		75
EXHIBIT D:	PREPARATION AND ANALYSIS METHODS		81
	I.	Introduction	83
	II.	Holding Times and Storage Requirements	85
	III.	Methodology and Data User Guide	87
	IV.	Sample Preparation	91
	V.	Sample Analysis	95
EXHIBIT E:	QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS		219
	I.	General QA/QC Practices	221
	II.	Specific QA/QC Procedures	223
	III.	Laboratory Evaluation Process	243
EXHIBIT F:	CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND STANDARD OPERATING PROCEDURES		245
	I.	Chain-of-Custody	247
	II.	Document Control	249
	III.	Standard Operating Procedures	253
EXHIBIT G:	GLOSSARY OF TERMS		257

PREFACE

The purpose of this contract is to provide the U.S. Environmental Protection Agency (EPA) with inorganic chemical analytical services using direct nebulization, inductively coupled plasma and hydride inductively coupled plasma emission spectroscopy (ICP and HYICP), graphite furnace and cold vapor atomic absorption spectroscopy (GFAA and CVAA), and specified cyanide, conductivity, and pH techniques for the analysis of high concentration field samples. The majority of these samples to be analyzed are from known or suspected hazardous waste sites and may contain potentially 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 and precautions to ensure the health and safety of its employees. The Contractor is responsible for providing a safe working environment and making its employees aware of the potential hazards of working with and analyzing these samples.

Procedures specified herein shall be used in the preparation and analysis of liquid, solid, and multiphase samples for the presence and quantitation of 22 metals, cyanide, conductivity, and pH. The Contractor shall employ safe handling procedures and generally accepted good laboratory practices in the performance of contract requirements and shall follow the quality assurance/quality control (QA/QC) program specified herein.

The data obtained under this contract will be used by the EPA to determine the existence and extent of threats to the public and the environment posed by hazardous waste disposal sites. The data may be used in civil and/or criminal litigation which requires the strictest adherence to chain-of-custody protocol, document control, and quality assurance procedures.

EXHIBIT A

SUMMARY OF REQUIREMENTS

EXHIBIT A

TABLE OF CONTENTS

		Page
SECTION I:	SUMMARY OF METHOD	3
SECTION II:	GENERAL REQUIREMENTS	5
SECTION III:	SPECIFIC REQUIREMENTS	7

SECTION I

SUMMARY OF METHOD

1. Purpose

1.1 Samples of industrial waste materials gathered in support of EPA investigations of disposal. handling and storage practices are subjected to limited chemical characterization using the procedures and methods prescribed herein. This characterization is not designed to define the total composition of the samples, but is designed essentially to look for specific constituents. The characterization is targeted to the analysis of the priority pollutants and additional inorganic parameters.

1.2 Samples may be obtained from drummed materials, waste pits or lagoons, piles of waste, tanker trucks, onsite tanks, or apparent contaminated soil areas.

1.3 The waste materials usually are industrial process waste, byproducts, raw materials, intermediates and contaminated products. Many of the samples may be spent oil, spent solvents, paint wastes, metal treatment wastes, and polymer formulations.

1.4 The methods are included for the determination of 22 metals, cyanide, conductivity, and pH. Also included is a phase separation method that is applied to samples prior to digestion and analysis. Each individual phase is digested and analyzed by the specific methods. (A phase being either water miscible, non-water miscible, or solid.)

2. Limitations

2.1 A detailed knowledge of the chemical and physical properties of samples submitted for analysis, as well as the behavior of analytes under specific conditions, are not available with the wide variety of materials that are submitted under this contract. Although the analytical methods contained herein have been shown to be quantitative for a large number of sample matrices, the unknown nature of the samples prior to characterization can cause problems in certain instances.

2.2 The elemental constituent analysis approach only analyzes 22 metals. Interferences from metals not included in this analysis which may cause either positive or negative biases will not be corrected by this approach. The recovery of certain metals from a sample matrix may be affected by the presence of other metals or by the form of the metal, which may not be readily detected.

3. Characterization

3.1 Corrosivity of a waste may be determined by testing for either pH or rate of steel corrosion. The pH of water extracted samples as determined herein does not classify a waste as a RCRA waste but instead is determined for informative purposes such as to aid in waste segregation.

3.2 Reactive wastes may be wastes from one of many groups including unstable materials (explosives), materials that undergo violent reactions with water (sodium metal) or without water (pyrophorics), and materials that generate toxic vapors/gases upon reaction with water (phosphides) or mildly acidic conditions (cyanide). The method for cyanide determination included here is a "total" method for cyanide amenable to distillation under strongly acidic conditions.

3.3 The identification of metal constituents, including priority pollutants, is part of the EPA determination of a toxic waste. This material is not a "toxic" waste in the normal usage of the word but instead is based on the potential for the hazardous constituents of the waste to leak out of the waste site (landfill, pond, etc.) and contaminate the soil and/or ground water.

SECTION II

GENERAL REQUIREMENTS

The Contractor shall employ procedures specified in this Statement of Work (SOW) for the preparation and analysis of high concentration samples that may or may not contain more than one phase (i.e., water miscible, non-water miscible, and solid) for the presence and quantitation of 22 metals, cyanide, conductivity, and pH.

Exhibit B contains all reporting and deliverables requirements for the contract, including copies of the data reporting forms and a Form Instruction Guide. Exhibit C contains the Contract Required Quantitation Limits (CRQLs) for all target analytes. Exhibit D contains the specific analytical procedures required, defines the specific application of these procedures, and contains the method specific QA/QC requirements of this contract. Exhibit E contains general and specific laboratory QA/QC requirements. Exhibit F contains chain-of-custody and document control requirements that the Contractor must follow in processing samples under this contract, and specifies requirements for written laboratory Standard Operating Procedures (SOPs). 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 definition, the glossary meaning shall be applicable.

A full sample analysis is defined as identification and quantitation of specific inorganic analytes in Exhibit C, in accordance with the methods in Exhibit D and the performance of related QA/QC procedures in Exhibits D and E.

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

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION III

SPECIFIC REQUIREMENTS

For each sample, the Contractor shall perform the following tasks:

1. Task I: **Receive and Prepare Hazardous Waste Samples.**

1.1 The Contractor shall receive and handle samples under the chain-of-custody and document control procedures described in Exhibit F. Sample receiving procedures listed in Task III (3) shall also be followed.

1.2 The Contractor shall separate multi-phase samples into single phase units and prepare each unit for analysis. If a sample consists of more than three phases, the Contractor shall contact the Sample Management Office (SMO) for further direction. The Contractor shall note that the identifiers for the phases shall follow a lowercase letter system in which the particular phase type is given a direct letter identifier and assigned a letter for each phase of that type. The Contractor shall use the following identifiers for this contract: water miscible, a "w" (e.g., wa, wb, wc); solid, a "c" (e.g., ca, cb, cc); and non-water miscible, an "n" (e.g., na, nb, nc). In the example above, the second letter of this system is used to identify the number of phases of this type for the sample (e.g., a equals 1, b equals 2, c equals 3). Each phase shall be considered a full sample analysis.

1.3 Exhibit D contains instructions and references for preparation and analyses of high concentration inorganic samples by ICP, HYICP, GFAA, CVAA, cyanide, conductivity, and pH methods. A schematic flow chart depicting the complete high concentration inorganics analytical scheme is presented in Section I of Exhibit D.

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

1.5 The Contractor shall be responsible for all necessary measures and precautions to ensure the health and safety of laboratory employees. The Contractor is advised that the samples received under this contract are usually from known or suspected hazardous waste sites and may contain high (e.g., greater than 15 percent) levels of inorganic and/or organic materials of a potentially hazardous nature and of unknown structure and concentration. All samples should be handled throughout the analysis with appropriate safety precautions.

2. Task II: **Analyze Samples for the Identification and Quantitation of Specific Inorganic Analytes.**

2.1 Samples prepared in Task I shall be analyzed by methods specified in Exhibit D for the target analytes listed in Exhibit C. The Contractor shall provide the required analytical expertise and instrumentation for analyses of target metals, cyanide, conductivity, and pH equal to or lower than the quantitation limits specified in Exhibit C. The Contractor shall meet the control limits also provided in Exhibit C for analysis of various QC samples and their specified methods.

2.2 The Contractor shall have sufficient analytical equipment and capability to meet all terms and conditions of the contract as specified by the following:

- Inductively coupled plasma (ICP) emission spectrophotometer with the capability to analyze metals sequentially or simultaneously, and hydride generation and analysis capabilities;

- Atomic absorption (AA) spectrophotometer equipped with a graphite furnace and cold vapor AA (or a specific mercury analyzer) analysis capabilities; and

- Analytical equipment/apparatus for analysis of cyanide, conductivity, and pH as described in Exhibit D.

2.3 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.

- 100 Samples/Month Capacity Requirements

Fraction	No. of Instrument (s)	Type of Instrument
ICP Metals	1	ICP Emission Spectrophotometer; with Hydride Manifold Accessory (if necessary)
GFAA Metals (if necessary)	1	Atomic Absorption Spectrophotometer with Graphite Furnace Atomizer
Mercury	1	Mercury Cold Vapor AA Analyzer or AA Instrument Modified for Cold Vapor Analysis
Cyanide	6 Distillation Units and 1 Photometer	See Cyanide Methods, Statement of Work Exhibit D, Section IV, Part G
pH	1	See pH Methods, Statement of Work Exhibit D, Section IV, Part A
Conductivity	1	See Conductivity Methods, Statement of Work Exhibit D Section IV, Part B

2.4 All samples shall be carried through the sample preparation procedure and then run undiluted. When an analyte concentration exceeds the calibrated or linear range, appropriate dilution and reanalysis of the prepared sample is required, as specified in Exhibit D. The dilution factor shall not bring the concentration below the CRQL. All dilutions must be taken from the original sample. Diluting previously diluted samples is not acceptable.

2.5 Exhibit D specifies the analytical procedures that shall be used. The identification and quantitation of all metals except mercury shall be accomplished using either ICP, HYICP, or GFAA methods specified in Exhibit D. The appropriate method must be selected to achieve the CRQL in Exhibit C. Mercury, cyanide, conductivity, and pH shall be analyzed by the individual procedures specified in Exhibit D.

2.6 For the purpose of this contract, a full sample analysis is defined as identification and quantitation of specific inorganic analytes in Exhibit C, in accordance with the methods in Exhibit D and the performance of related QA/QC procedures in Exhibits D and E. Duplicate sample, laboratory control sample, and spike sample analyses shall each be considered a separate full sample analysis. A sample may consist of more than one phase (e.g., water miscible, non-water miscible, and solid) contained inside appropriate receptacles. More than one container may be received for a single sample. All other QA/QC requirements are considered an inherent part of this contract and are included in the contract sample unit price.

3. Task III: **Perform Required Quality Assurance/Quality Control Procedures**

3.1 All QA/QC procedures prescribed in Exhibits D and E shall be strictly adhered to by the Contractor, including daily or (as required) more frequent use of standard reference solutions from EPA, the National Institute of Standards and Technology (NIST), or secondary standards traceable thereto. Records documenting the use of the procedures shall be maintained in accordance with the document control procedures in Exhibit F, and shall be reported in accordance with Exhibit B requirements.

3.2 The Contractor shall establish a Quality Assurance Program (QAP) with the objective of providing sound analytical chemical measurements. This program shall incorporate QC procedures, any necessary corrective action taken, all documentation required during data collection, and the quality assessment measures performed by management to ensure acceptable data production.

3.3 Additional QA/QC shall be required on a quarterly basis in the form of a Performance Evaluation (PE) samples submitted by EPA for Contractor analysis, and in the form of verification of instrument parameters, as described in Exhibit E.

3.4 A Laboratory Control Sample (LCS) shall be analyzed to assure that the operating parameters of the analytical instrumentation and analytical procedures from sample receipt through identification and quantitation are capable of producing reliable data. The Contractor shall analyze the LCS concurrently with the analysis of the samples in the SDG.

3.5 EPA has provided formats to the Contractor for the reporting of data (Exhibit B). The Contractor shall be responsible for completing and returning analysis data sheets in the format specified in this SOW within the time specified in the Contract Performance/Delivery Schedule.

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

3.5.2 Computer generated forms may be submitted in the hardcopy data package(s) provided that the forms are identical to the EPA FORMAT. This means that the order of data elements is the same as on each EPA required form, including form numbers, titles. page numbers, header information, columns, and lines. The only exception to this requirement shall be the use of a different font to conform to a laboratory's printer configuration.

3.6 The Contractor shall designate and utilize key personnel listed below to perform the minimum functional requirements necessary to meet the terms and conditions of this contract. The minimum education and experience requirements for these functions are identified in Bidder Responsibility. Attachment C of this contract. The Contractor must report changes in key personnel by submitting resumes for replacement personnel along with quarterly delivery of Quarterly Verification of Instrument Parameters Report to the Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) and SMO. The EPA reserves the right to review personnel qualifications and expertise. The following positions are considered key personnel for this contract:

- Laboratory Supervisor;
- QA Officer;
- Inductively Coupled Plasma (ICP) Spectroscopist;
- Atomic Absorption (AA) Spectroscopist;
- Inorganic Sample Preparation Specialist;
- Classical Wet Chemistry (Cyanide) Analyst; and
- Inorganic Chemist (Backup).

NOTE: The Contractor shall also designate a sample custodian and a document control officer.

3.7 The Contractor shall respond within 10 days to requests from data recipients for additional information or explanations that result from the Government's inspection activities.

3.8 The Contractor shall retain unused sample volumes and used sample containers for a period of 60 days after data submission.

3.9 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 strictly being followed. This documentation shall be reported in the Complete SDG File (see Exhibit B).

3.10 Sample shipments to the Contractor's facility will be scheduled and coordinated by SMO, acting

on behalf of the EPA 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.

3.10.1 If there are problems with samples (e.g., broken or leaking containers) or sample documentation/paperwork (e.g., missing, incomplete, or conflicting Traffic Reports), then the Contractor shall contact SMO immediately for resolution. The Contractor shall notify SMO immediately regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall notify SMO personnel in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

3.11 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. 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 (SDGs). A 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 (said period beginning with the receipt of the first sample in the SDG).

3.12 Data for all samples in a 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 date that the last sample in the SDG is received.

3.13 The Contractor is responsible for identifying each SDG as samples are received, and properly documenting samples (see Exhibit B) and communicating with SMO personnel.

3.14 Each sample received by the Contractor will be labeled with an EPA sample number and accompanied by a Traffic Report (TR) form bearing the sample number and descriptive information regarding the sample. The Contractor shall complete and sign the TR, recording the date of sample receipt and sample condition upon receipt for each sample container.

3.15 The Contractor shall submit signed copies of TRs for all samples in a SDG to SMO within three calendar days following receipt of the last sample in the SDG. TRs shall be submitted in SDG sets (i.e., all TRs for a SDG shall be clipped together) with a SDG cover sheet containing information regarding the SDG, as specified in Exhibit B.

3.16 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 and correspondence.

3.17 Samples will be routinely 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.

3.18 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.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

EXHIBIT B

TABLE OF CONTENTS

		Page
SECTION I:	Contract Reports/Deliverables Distribution	15
SECTION II:	Report Descriptions and Order of Data Deliverables	17
SECTION III:	Form Instruction Guide	27
SECTION IV:	Data Reporting Forms	55

SECTION I

CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

The following table summarizes the contract reporting and deliverables requirements specified in the Contract Schedule and includes the distribution of each deliverable. **NOTE:** Specific recipient names and addresses are subject to change during the term of the contract. The EPA Administrative Project Officer (APO) or SMO will notify the Contractor in writing of such changes when they occur.

Item	No. of Copies	Schedule and Delivery	Distribution		
			(1)	(2)	(3)
Updated SOPs	2	45 days after contract award		X	X
*Sample Traffic Reports	1	*** 3 days after receipt of last sample in Sample Delivery Group (SDG)	X		
**Sample Data Package	2	35 days after receipt of last sample in SDG	X	X	
Complete SDG File	1	35 dyas after data receipt of last sample in SDG			X
*Quarterly and Annual Verfication of Parameters	2	15th day of January, April, July, October	X	X	
****Quality Assurance Plan	1	Submit copy within 7 days of written request by APO			

Distribution

(1) Sample Management Office (SMO)
(2) Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV)
(3) USEPA Region

* 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 and not exceeding 20 samples. Data for all samples in the SDG are due concurrently. (See Exhibit A, Task III, for further description.)

**** See Exhibit E for description.

NOTE: As specified in the Contract Schedule (Government Furnished Supplies and Materials), unless otherwise instructed by SMO, the Contractor shall dispose of unused sample volumes 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 22314

(2) USEPA Environmental Monitoring
Systems Laboratory (EMSL-LV)
P. O. Box 15027
Las Vegas, NV 89114
ATTN: Data Audit Staff

For overnight delivery service, use street address:

944 E. Harmon, Executive Center
Las Vegas, NV 89109
ATTN: Data Audit Staff

(3) USEPA REGIONS:

SMO, acting on behalf of the EPA APO, 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.

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

The Contractor shall provide reports and other deliverables according to the schedule specified in Section F of the contract, Deliveries or Performance. The required content and form of each deliverable is described in this Exhibit.

All reports and documentation must be:

- Legible;
- Clearly labeled and completed in accordance with instructions in this Exhibit;
- Arranged in the order specified in this Section;
- Paginated; 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.

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, the data shall be clearly marked as "ADDITIONAL DATA" and shall be sent to all three contractual data recipients (SMO, EMSL-LV, and Region). A cover letter shall be included that describes what data are being delivered, to which EPA Case(s) the data pertain, and who requested the data.

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). In all three instances, the data must be accompanied by a color-coded Cover Sheet (Laboratory Response To Results of Contract Compliance Screening) provided by SMO.

Section III of this Exhibit contains instructions to the Contractor for properly completing all data reporting forms to provide the EPA with all required data. Section IV of this Exhibit contains the required Inorganic Analysis Data Reporting Forms in EPA-specified formats.

Descriptions of the requirements for each deliverable item cited in the Contract Performance/Delivery Schedule (Section F.1) are specified as follows in 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.

1. Updated Standard Operating Procedures

1.1 The Contractor shall submit updated copies of all required Standard Operating Procedures (SOPs) that were submitted with the preaward Performance Evaluation (PE) sample results. The updated SOPs must address any and all issues of laboratory performance and operation identified through the review of the Performance Evaluation sample data and the evaluation of Bidder-Supplied Documentation.

1.2 The Contractor must supply SOPs for the following:

- Sample receipt and logging;

- Sample and extract storage area;
- Evidentiary SOPs;
- Preventing sample contamination;
- Security for laboratory and samples;
- Traceability/equivalency of standards;
- Maintaining instrument records and bound logbooks;
- Glassware cleaning;
- Technical and managerial review of laboratory operation and data package preparation;
- Internal review of contractually required QA/QC data for each individual data package;
- Sample analysis, data handling, and data reporting;
- Chain-of-custody and document control, including SDG file preparation;
- Sample data validation/self-inspection system; and
  - Data flow and chain-of-command for data review;
  - Procedures for measuring precision and accuracy;
  - Evaluation parameters for identifying systematic errors;
  - Procedures to assure that hardcopy data are complete and compliant with the requirements in Exhibit B;
  - Demonstration of internal QA inspection procedure (demonstrated by supervisory sign-off on personal notebooks, internal PE samples, etc.);
  - Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas);
  - Demonstration of problem identification, corrective actions, and resumption of analytical processing resulting from internal audit (i.e., QA feedback); and
  - Documentation of audit reports (internal and external), response, corrective action, etc.
- Data Handling.
  - <u>Data Management</u>

    a. Data Management procedures defined as written procedures that are clearly defined for all databases and files used to generate or re-submit deliverables specifying the acquisition or entry, update, correction, deletion, storage, and security of computer readable data and files. Key

areas of concern include: system organization including personnel and security, documentation, operations, traceability, and quality control.

- Data manually entered from hardcopy must be quality controlled and error rates estimated.

- Data entry rates must be estimated and recorded on a monthly basis by re-entering a statistical sample of the data entered calculating discrepancy rates by data element.

- The record of changes in the form of corrections and updates to data originally generated, submitted, and/or re-submitted must be documented to allow traceability of updates. Documentation must include the following information for each change:

  a. Justification or rationale for the change;

  b. Initials of the person making the change or changes. Data changes must be implemented and reviewed by a person or group independent of the source generating the deliverables;

  c. Change documentation must be retained according to the schedule of the original deliverable;

  d. Resubmitted deliverables must be re-inspected as a part of the laboratory's internal inspection process prior to submission. The entire deliverable and not just the changes must be re-inspected;

  e. The laboratory manager must approve changes to originally submitted deliverables; and

  f. Documentation of data changes may be requested by laboratory auditors.

- Life Cycle Management procedures must be applied to computer systems 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 user's manual and an operations and maintenance manual.

- Individual(s) responsible for the following functions must be identified:

  a. System operation and maintenance including documentation and training: and

  b. Database integrity including data entry, data updating and QC.

- Data and system security, backup, and archiving.

2. Sample Traffic Reports

2.1 The original Sample Traffic Report (TR) page marked "Lab Copy for Return to SMO" shall be submitted to SMO with laboratory receipt information and signed in original Contractor signature. for each sample in the SDG.

2.2 TRs shall be submitted in SDG sets (i.e., TRs for all samples in a SDG shall be clipped together), with a SDG Cover Sheet attached.

2.3 The SDG Cover Sheet shall contain the following items:

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

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample receive would be the lowest sample number (considering both alpha and numeric designations), and the "last" sam received would be the highest sample number (considering both alpha and numeric designations). For exam AH230 is a lower sample number than AI200, as H precedes I in the alphabet.

2.4 Each TR shall be clearly marked with the SDG Number, the sample number of the first sample in t SDG. This information should be entered below the Lab Receipt Date on the TR. The TR for the last san received in the SDG shall be clearly marked "SDG - FINAL SAMPLE."

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

3. Sample Data Package

3.1 The sample data package shall be complete and consecutively paginated, and shall include data for analysis of all samples in one SDG, including analytical and field samples, sample reanalyses, blanks, spikes, duplicates, and laboratory control samples. The sample data package is divided into six units as follows:

- Cover Page;
- Sample Data (Sample results including the PES);
- Quality Control Summary;
- Raw Data;
- Preparation Logs; and
- Sample Traffic Reports

3.1.1 Cover Page

3.1.1.1 This document shall be clearly labeled "Cover Page". The Cover Page shall contain: laboratory name; laboratory code; contract number; Case No.; SDG No.; SOW number (appears on cover page of SOW); EPA sample numbers in alphanumeric order, showing EPA sample numbers cross-referenced with laboratory ID numbers; comments, describing in detail any problems encountered both technical and administrative, the corrective action taken, and resolution performed for all of the samples in the SDG; and completion of the statement on use of ICP background and interelement corrections for the samples.

3.1.1.2 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, excluding the conditions detailed above. Release of the data contained in this hardcopy data package has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature." This statement shall be followed by the signature of the Laboratory Manager or the Manager's designee with a typed line below it containing the signator's name and title and the date of signature.

3.1.1.3 In the event that 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.

3.1.2 Sample data shall be submitted with FORM I-HCIN, the High Concentration Inorganic Analysis Data Sheet, for all samples in the SDG and shall be arranged in increasing alphanumeric EPA sample number order.

3.1.3 Quality Control Summary

3.1.3.1 The quality control summary shall contain the following forms: NOTE: If more than one form is necessary, duplicate forms must be arranged in chronological order.

- Initial and Continuing Calibration Verification [FORM II - HCIN]
- CRQL Standards/Linear Range Standards [FORM III - HCIN]
- Blanks [FORM IV - HCIN]
- ICP Interference Check Sample [FORM V - HCIN]
- Spike Sample Recovery [FORM VI - HCIN]
- Analytical Spike Sample Recovery [FORM VII - HCIN]
- Duplicates [FORM VIII - HCIN]
- Laboratory Control Sample [FORM IX - HCIN]
- Standard Addition Results [FORM X - HCIN]
- Method Detection Limits [FORM XI - HCIN]
- ICP Interelement Correction Factors (Annual) [FORM XII - HCIN]
- Phase Separation Log [FORM XIII - HCIN]
- Preparation Separation Log [FORM XIV - HCIN]
- Analysis Run Log [FORM XV - HCIN]

3.1.4 Raw Data

3.1.4.1 For each reported value, the Contractor shall include all raw data from the instrument used to obtain the sample values (except for raw data for quarterly verifications of instrument parameters). Raw data shall contain all instrument readouts used for the sample results, including those readouts that may fall below the Method Detection Limit (MDL). All AA and ICP instruments must provide a legible hardcopy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the direct sequential instrument readout must be included. A hardcopy of the direct instrument readout for cyanide must be included if the instrumentation has the capability. A stripchart is required for mercury.

3.1.4.2 The order of raw data in the data package shall be as follows: ICP, HYICP, GFAA, mercury, cyanide, conductivity, and pH. The raw data shall be arranged in alphabetical order per element (excluding ICP analysis) and in chronological order as listed in section 3.1.3.1 for each method used. All raw data must include intensities for ICP and absorbances for AA, wherever possible.

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

- Calibration standards, including source and preparation date.
- Initial and continuing calibration blanks and preparation blanks.
- Initial and continuing calibration verification standards, interference check samples, CRQL standard, and linear range standard.
- 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, then a general statement outlining these parameters is sufficient.
- Duplicates.
- Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, then a general statement outlining these parameters is sufficient.
- 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.
- Date and EPA Sample Number for ICP, HYICP, and GFAA analyses clearly and sequentially identified on the raw data.
- All calculations for sample and analytical spike data, including percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, slope and y intercept of linear fit, and final sample concentration (standard addition concentration).
- Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide time of analysis, the time and date must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and linear range analysis standards.
- Integration times for CVAA analysis.

3.1.5 Fusion, Digestion and Distillation Logs

3.1.5.1 Logs shall be submitted in the following order: fusion logs, digestion logs for ICP, HYICP, GFAA and mercury preparations, followed by a copy of the distillation logs for cyanide. These logs must include the following:

- Date of preparation;

Table 1

Codes for Labeling Raw Data

Sample	XXXXXXyy
Duplicate	XXXXXXyyD
Sample Spike	XXXXXXyyS
Serial Dilution	XXXXXXyyL
Analytical Spike	XXXXXXyyA
MSA:	
Zero Addition	XXXXXXyy0
First Addition	XXXXXXyy1
Second Addition	XXXXXXyy2
Third Addition	XXXXXXyy3
Instrument Calibration Standards:	
ICP	S or S0 for blank standard
Atomic Absorption and Cyanide	S0, S10,...etc.
Initial Calibration Verifications	ICV
Initial Calibration Blank	ICB
Continuing Calibration Verifications	CCV
Continuing Calibration Blanks	CCB
Interference Check Samples:	
Solution A	ICSA
Solution AB	ICSAB
CRQL Standard for ICP	CRI
Laboratory Control Samples	LCS
Preparation Blank	PB
Linear Range Analysis Standard	LRS

Notes:

1. When an analytical spike or MSA is performed on a sample, 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 "XXXXXXyyDA".
2. The numeric suffix that follows the "S" suffix for the standards indicates the true value for the concentration of the standard in $\mu g/L$.
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. yy = phase identifier.

- Sample weights and volumes;
- Sufficient information to identify unequivocally which QC samples (i.e., laboratory controlsample, preparation blank) correspond to each batch prepared; and
- Comments describing any significant sample changes or reactions which occur during preparation.

3.1.6 Sample Traffic Report

3.1.6.1 A legible copy of the Sample TRs and SDG Cover Sheet shall be submitted as described in Section 2 of this Exhibit for all of the samples in the SDG. The TRs shall be arranged in increasing EPA sample number order, considering both alpha and numeric designations.

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

4.1 The reporting of analytical results for Intercomparison Study/Performance Evaluation (PE) sample analyses includes all requirements specified in item 3.1.1 for reporting of sample data. PE samples shall be carried through the exact same process as analytical and field samples.

5. Complete SDG File

5.1 The Complete SDG File (CSF) package includes all laboratory records received or generated for a specific Case that have not been previously submitted to EPA as a deliverable. These items shall be submitted along with their Document Inventory Sheet FORM HDC-2 (see Exhibit F for description of document numbering and inventory procedure). These items include, but are not limited to: sample tags, custody records, sample tracking records, analysts' logbook pages, bench sheets, instrument readout records, computer printouts, raw data summaries, instrument logbook pages (including instrument conditions), correspondence, and the document inventory.

5.2 Shipment of the CSF package by first class mail, overnight courier, priority mail or equivalent is acceptable. Custody seals, which are provided by EPA, shall be placed on shipping containers, and a document inventory and transmittal letter shall be included. The Contractor is not required to maintain any documents for a sample Case after submission of the Complete SDG File package; however, the Contractor should maintain a copy of the document inventory and transmittal letter.

6. Quarterly and Annual Verification of Instrument Parameters

6.1 The Contractor shall perform and report quarterly verification of MDLs by methods specified in Exhibits D and E for each type and model number of instrument used under this contract. For the ICP instrumentation and methods, the Contractor shall also perform and report annual interelement correction factors (including method of determination), wavelengths used and integration times. Annual Verification of Instrument Parameters forms for the current year shall be submitted in each sample data package, using FORM XII-HCIN. Submission of Quarterly Verification of Instrument Parameters shall include the raw data used to determine those values reported.

7. Quality Assurance Plan (QAP)

7.1 The Contractor shall prepare a written Quality Assurance Plan (QAP) 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 established corrective action procedures which keep the analytical process reliable; and document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

7.2 The QAP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA/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.

SECTION III

FORM INSTRUCTION GUIDE

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

- General Information and Header Information
- Cover Page - [COVER PAGE - HCIN]
- Analysis Data Sheet [FORM I - HCIN]
- Initial and Continuing Calibration Verification [FORM II - HCIN]
- CRQL Standards/Linear Range Standards [FORM III - HCIN]
- Blanks [FORM IV - HCIN]
- ICP Interference Check Sample [FORM V - HCIN]
- Spike Sample Recovery [FORM VI - HCIN]
- Analytical Spike Sample Recovery [FORM VII - HCIN]
- Duplicates [FORM VIII - HCIN]
- Laboratory Control Sample [FORM IX - HCIN]
- Standard Addition Results [FORM X - HCIN]
- Method Detection Limits (Quarterly) [FORM XI - HCIN]
- ICP Interelement Correction Factors (Annual) [FORM XII - HCIN]
- Phase Separation Log [FORM XIII - HCIN]
- Preparation Log [FORM XIV - HCIN]
- Analysis Run Log [FORM XV - HCIN]
- Sample Log-In Sheet [FORM HDC-1]
- Document Inventory Sheet [FORM HDC-2]

1. General Information and Header Information

1.1 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. Multiple forms cannot be submitted in place of one form if the information on those forms can be submitted on one form.

1.2 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 five, drop it (round down). If the figure is greater than five, drop it and increase the last digit to be retained by one (round up). If the figure following the last digit to be retained equals five and there are no digits to the right of the five or all digits to the right of the five 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 of Terms (Exhibit G).

1.3 All characters which appear on the data reporting forms presented in the contract 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 Project Officer. The names of the various fields and analytes (i.e., "Lab Code", "Aluminum") on the forms must appear as they do on the forms (Section IV), except that the use of uppercase and lowercase letters is optional.

1.4 All alphabetic entries made onto the forms by the Contractor must be in ALL UPPERCASE letters (i.e., "LOW", not "Low" or "low") except phase identifiers (i.e., "wa", not "Wa" or "WA").

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

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

1.5.2 The "Contract" is the number of the EPA contract, including hyphens, under which the analyses were performed.

1.5.3 The "Lab Code" is an alphabetic abbreviation of up to six characters, assigned by the EPA, to identify the laboratory and aid in data processing. This lab code shall be assigned by the EPA at the time a contract is awarded, and must not be modified by the Contractor, except at the direction of EPA. If a change of name or ownership occurs at the laboratory, the lab code will remain the same until the Contractor is directed by the EPA to use another lab code assigned by the EPA.

1.5.4 The "Case No." is the EPA-assigned Case number (up to five characters) associated with the sample and recorded on the TR.

1.5.5 The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services (SAS). 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, then 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 a SDG may have a SAS No., while others may not.

1.5.6 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.

1.6 EPA Sample Number

1.6.1 The EPA Sample Number is the unique identifying number given in the TR that accompanied that sample. This number is assigned by the EPA and it must be used exactly as assigned.

1.6.2 The "EPA SAMPLE NO." must be entered on several of the forms. 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 the "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.

1.6.3 All field samples and quality control samples associated with field samples must be identified with an EPA Sample Number.

1.6.4 The phase suffix is assigned to each phase by appending a unique two letter identifier with the first letter identifying the phase, and the second identifying the number of phases of that type. These identifiers shall be only in lower case letters. These identifiers are as follows: a "w" for water miscible, "c" for solid, and "n" for non-water miscible with the second values ranging from a through z. If the sample consists of a water miscible phase, then the phase suffix must be a "wa". If the sample consists of more than one phase such as a water miscible phase, a solid phase, and a non-water miscible phase, then the water miscible phase suffix must be a "wa", the solid phase suffix must be a "ca", and the non-water miscible suffix must be a "na".

1.6.5 In addition, the sample suffix and quality control sample abbreviations listed in Table 1, Section II of this Exhibit, must be used as appropriate.

1.7 All results must be transcribed to FORMs II-XIII from the raw data with the specified number of decimal places that are described in this Exhibit. 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
5.9	6.3	5.900
5.99653	6.3	5.997
95.99653	6.3	95.997
995.99653	6.3	996.00
9995.996	6.3	9996.0
99995.9	6.3	99996.
999995.9	6.3	invalid

NOTE: 6.3 stands for a maximum of six significant figures and up to three decimal places.

1.8 Before evaluating a number for being in control or out of control in relationship to 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 ± 10 percent of the true value. A percent recovery value of 110.4 would be considered in control while a 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 110.55 would be out of control.

2. Cover Page [Cover Page - HCIN]

2.1 This form is used to list all billable sample phases analyzed within an SDG, 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.

2.2 Complete the header information according to the previous instructions.

2.3 The "SOW No." is the EPA-designated number that indicates the Statement of Work (SOW) under which analyses in the data package have been performed. The SOW No. appears on the cover of the contract Statement of Work. For samples analyzed using this SOW, enter IHC01.3 for "SOW No."

2.4 Under "EPA Sample No.", enter up to 10 characters for the EPA Sample No. (including spikes and duplicates) for each phase that required analysis 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 using the EBCDIC convention. Thus, if MAB123A 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 listed below it would be in ascending sequence - MAB124A, MAB124B, MAB125A, MAC111A, MA1111A, MA1111AD, etc.

2.5 All EPA Sample Numbers must be listed in ascending alphanumeric order, continuing to the following Cover Page if applicable.

2.6 Under "Lab Sample ID", a laboratory sample ID (up to 10 characters) may be entered for each associated EPA Sample No. If a Lab Sample ID is entered, it must be entered identically (for each EPA Sample No.) on all associated data.

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

2.8 Under "Comments", enter any problems encountered, both technical and administrative, the corrective action taken, and resolution performed for all of the samples in the SDG.

2.9 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.

3. Analysis Data Sheet [FORM I - HCIN]

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

3.2 Complete the header information according to the header instructions and as follows.

3.3 For "Phase", enter the phase that describes the sample. The phase may be only "SOLID", "WATER MISCIBLE", or "NON-WATER MISCIBLE". Additional descriptions that can better characterize the sample may be listed in the comments section.

3.4 For "Water Miscibility", enter "YES" if the phase of the sample listed is water miscible, "NO" if the phase is non-water miscible and "PART" if the phase is partially water miscible. If the sample phase is not a liquid, then leave the field empty.

3.5 For "Percent", enter the percent (to two decimal places) of total sample that the reported phase constitutes of the total sample weight calculated according to equation B-1:

$$Percent = \frac{Phase\ Weight\ in\ Grams}{Total\ Sample\ Weight\ in\ Grams} \times 100 \qquad \text{B-1}$$

NOTE: The percent listed on the form for a phase of a sample must equal that which is listed for that phase on FORM XIII-HCIN.

3.6 For "pH", enter the pH value obtained (to the nearest tenth of a whole number) for the water miscible phase listed on the form.

3.7 For "Conductivity", enter the conductivity value (to the nearest whole number) for the water miscible phase listed on the form.

3.8 For "Lab Sample ID", enter the laboratory sample ID for the phase listed on the form, as listed on the Cover Page.

3.9 For "Date Received" enter the date (formatted MM/DD/YY) the sample was received at the laboratory, as recorded on the TR, i.e., the Validated Time of Sample Receipt (VTSR).

3.10 Under the column labeled "CONCENTRATION", if the analytical result is greater than or equal to the Method Detection Limit (MDL), report the result. If the result is lower than the MDL, report the MDL value.

3.11 Analytical results must be reported to two significant figures in mg/Kg if the result value is less than 10, and to three significant figures if the result value is greater than or equal to 10.

3.12 The requirement for reporting results to two or three significant figures applies to FORM I-HCIN only. Follow the specific instructions for reporting all other results on required forms as described in this Exhibit.

3.13 Under the columns labeled "C", "Q", and "M", enter result qualifiers as identified in items 3.14.1, 3.14.2, and 3.14.3. If additional qualifiers are used, their explicit definitions must be included on the Cover Page in the Comments section.

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

3.14.1 C (Concentration) qualifier: Enter "B" if the reported value was obtained from a reading that was less than the Contract Required Quantitation Limit (CRQL) but greater than or equal to the MDL. Enter "U" if the reported value was obtained from a reading that was less than the MDL.

3.14.2 Q (Quality Control) qualifier: Specified entries and their meanings are as follows:

E	-	The reported value is estimated because of the presence of interference;
I	-	The sum of the values of the interference correction(s) is greater than the result concentration;
M	-	Duplicate injection/exposure precision not met;
N	-	Spiked sample recovery not within control limits;
S	-	The reported value was determined by the Method of Standard Additions (MSA).;
*	-	Duplicate analysis not within control limits; and
+	-	Correlation coefficient for the MSA is less than 0.995.

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

3.14.3 M (Method) qualifier: Enter, as appropriate, the following:

- "P" for ICP;
- "H" for HYICP;
- "F" for Graphite Furnace AA;
- "CV" for Manual Cold Vapor AA;
- "AV" for Automated Cold Vapor AA;
- "AS" for Semi-automated Spectrophotometric;
- "C" for Manual Spectrophotometric; and
- "NR" if the analyte is not required to be analyzed.

3.15 A brief physical description of the sample must be reported in the fields for "Color", "Clarity", "Texture", "Viscosity", and "Artifacts". For liquid samples, report color, clarity, and viscosity. For solid samples, report color, texture and artifacts.

3.16 Listed below are the only descriptive terms available for the specified criteria:

- Color — red, blue, yellow, green, orange, violet, white, colorless, brown, grey, or black;

- Clarity clear, cloudy, or opaque;
- Viscosity nonviscous (similar to water) or viscous; and
- Texture fine (powdery), medium (sand), or coarse (large crystals or rocks).

3.17 If artifacts are present, enter "YES" in the artifacts field and describe the artifacts in the Comments field. If artifacts are not present, enter "NO".

3.18 Under "Comments", enter any sample-specific comments concerning the analyte results and note any significant changes that occurred during sample analysis (i.e., MSA determination, interferences), both technical and administrative, the corrective action taken, and resolution performed for the sample in the SDG.

4. Initial and Continuing Calibration Verification [FORM II - HCIN]

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

4.2 Complete the header information according to the header instructions and as follows.

4.3 Enter the "Initial Calibration Source" (12 characters maximum) and the "Continuing Calibration Source" (12 characters maximum). Enter "EPA-LV" or "EPA-CI" to indicate EPA EMSL-Las Vegas or EMSL-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.

4.4 Use additional copies of FORM II-HCIN if more calibration sources were used.

4.5 Under "WAVE", enter the number of the wavelength for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

4.6 Under "INITIAL CALIBRATION True", enter the true concentration (in mg/L, to three decimal places) of each analyte in the Initial Calibration Verification Solution.

4.7 Under "INITIAL CALIBRATION Found", enter the most recent found concentration (in mg/L, to three decimal places), of each analyte measured in the Initial Calibration Verification Solution.

4.8 Under "INITIAL CALIBRATION % R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-2:
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.

$$\% R = \frac{Found\ (ICV)}{True\ (ICV)} \times 100 \qquad \text{B-2}$$

4.9 Under "CONTINUING CALIBRATION True", enter the true concentration (in mg/L, to three decimal places) of each analyte in the Continuing Calibration Verification Solution.

4.10 Under "CONTINUING CALIBRATION Found", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the Continuing Calibration Verification Solution.

NOTE: 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.

4.11 If more than one FORM II-HCIN 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.

4.12 Under "CONTINUING CALIBRATION % R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-3:

$$\% R = \frac{Found\ (ICV)}{True\ (ICV)} \times 100 \qquad \text{B-3}$$

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.

NOTE: 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.

4.13 Under "M", enter the method used as in item 3.14.3.

4.14 If more than one wavelength is used to analyze an analyte, then submit additional copies of FORM II-HCIN as appropriate.

4.15 The order of reporting ICVs and CCVs for each analyte must follow the chronological order in which the standards were run starting with the first FORM II-HCIN and moving from the left to the right continuing to the following FORM II-HCIN as appropriate. For instance, the first ICV for all analytes must be reported on the first FORM II-HCIN. In a run where three CCVs were analyzed, the first CCV must be reported in the left CCV column on the first FORM II-HCIN 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 II-HCIN. On the second FORM II-HCIN, 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 II-HCIN and the CCVs follow in the same fashion as explained before.

4.16 In the case where more than one wavelength is used for an analyte in the SDG, all ICV and CCV results of the longest wavelength from all runs must be reported before proceeding to report the results of the second wavelength used and so on.

4.17 Under "Comments", enter any ICV and CCV specific comments concerning the analyte results, any significant problems encountered during the ICV and CCV analysis (i.e., percent recovery outside the control limits, interferences), both technical and administrative, the corrective action taken, and resolution performed for the ICV and CCV.

5. Contract Required Quantitation Limit Standards/Linear Range Standards [FORM III-HCIN]

5.1 **Contract Required Quantitation Limit Standard**

5.1.1 This form is used to report analyte recoveries from analyses of the Contract Required Quantitation Limit (CRQL) Standards.

5.1.2 Complete the header information according to the header instructions and as follows.

5.1.3 Under "CRQL", enter the source of the CRQL Standard for ICP, HYICP, GFAA, cyanide, and mercury analyses in their respective fields (12 characters maximum each), as explained in item 4.3.

5.1.4 Under "WAVE", enter the wavelength number as explained in item 4.5.

5.1.5 Under "INITIAL True", enter the true concentration (in mg/L, to three decimal places) of each analyte in the CRQL Standard Source Solution that was analyzed for analytical samples associated with the SDG.

5.1.6 Under "INITIAL Found", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the CRQL Standard Solution analyzed at the beginning of each run.

5.1.7 Under "INITIAL % R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-4:

$$\% R = \frac{\textit{Found Initial CRQL Standard}}{\textit{True CRQL Standard}} \times 100 \qquad \text{B-4}$$

5.1.8 Under "FINAL Found", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the CRQL Standard Solution analyzed at the end of each run.

5.1.9 Under "FINAL % R", enter the value (to the nearest whole number) of the percent recovery computed according to the equation B-5:

$$\% R = \frac{\textit{Found Final CRQL Standard}}{\textit{True CRQL Standard}} \times 100 \qquad \text{B-5}$$

NOTE: For every initial solution reported there must be a final one. However, the opposite is not true. If a CRQL Standard was required to be analyzed in the middle of a run (to avoid exceeding the eight-hour limit), it must be reported in the "FINAL Found" section of this form.

5.1.10 Under "M", enter the method used as in item 3.14.3

5.1.11 If more CRQL standards analyses were required or analyses were performed using more than one wavelength per analyte, submit additional copies of FORM III-HCIN in the appropriate order.

5.1.12 The order of reporting CRQL standards for each analyte must follow the chronological order in which the standards were run starting with the first FORM III-HCIN and continuing to the following FORM III-HCIN 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.

5.1.13 Under "Comments", enter any CRQL-specific comments concerning the analyte results, any significant problems encountered during the CRQL standard analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the standard.

5.2 **Linear Range Standard**

5.2.1 This form is used to report analyte recoveries from the quarterly analysis of the Linear Range Standards (LRSs).

5.2.2 Complete the header information according to the header instructions and as follows.

5.2.3 Under "LRS", enter the source of the Linear Range Standards for ICP and HYICP analyses in their respective fields (12 characters maximum each), as explained in item 4.3.

5.2.4 For "Date", enter the date formatted (MM/DD/YY) on which the linear ranges were determined for use. This date must not exceed the date of analysis by ICP or HYICP in the SDG data package and must not precede the analysis date by more than three calender months.

5.2.5 Under "True", enter the true concentration (in mg/L, to three decimal places) of each analyte in the LRS Source Solution that was analyzed for the three calendar months.

5.2.6 Under "Found", enter the found concetration (in mg/L, to three decimal places) of each analyte measured in the LRS Source Solution that was analyzed for the three calendar months.

5.2.7 Under "% R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-6:

$$\% R = \frac{Found\ (LRS)}{True\ (LRS)} \times 100 \qquad \text{B-6}$$

Note: Any measurement in the SDG data package at or below the found concentration is within linear range. Any measurement above it is out of linear range, and thus, is an estimated value and must be diluted into linear range.

5.2.8 If more LRS analyses were required or analyses were performed using more than one wavelength per analyte, submit additional copies of FORM III-HCIN in the appropriate order.

5.2.9 Under "M", enter the method used as in item 3.14.3.

5.2.10 The order of reporting the LRS for each analyte must follow the chronological order in which the standards were run starting with the first FORM III-HCIN and continuing to the following FORM III-HCIN as appropriate. If multiple wavelengths are used for one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

5.2.11 Under "Comments", enter any LRS-specific comments concerning the analyte results, any significant problems encountered during the LRS analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the standard.

6. Blanks [FORM IV - HCIN]

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

6.2 Complete the header information according to the header instructions and as follows.

6.3 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

6.4 Under "INITIAL CALIB. BLANK", enter the concentration (in mg/L, to three decimal places) of each analyte in the most recent ICB.

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

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

6.7 Under "CONTINUING CALIBRATION BLANK 1", enter the concentration (in mg/L, to three decimal places) of each analyte detected in the first required CCB analyzed after the ICB. Enter any appropriate qualifier, as explained for the "Initial Calibration Blank", in the "C" qualifier column immediately following the "CONTINUING CALIBRATION BLANK 1" column.

6.8 If only one CCB 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 CCB were analyzed, then complete additional copies of FORM IV-HCIN as appropriate.

6.9 Under "PREPARATION BLANK", enter the concentration (in mg/Kg, to three decimal places) of each analyte in the Preparation Blank. Enter any appropriate qualifier, as explained for the Initial Calibration Blank, in the "C" qualifier column immediately following the "PREPARATION BLANK" column.

6.10 Under "M", enter the method used, as explained in item 3.14.3.

6.11 If more than one wavelength is used to analyze an analyte, submit additional copies of FORM IV-HCIN as appropriate.

6.12 The order of reporting ICBs and CCBs for each analyte must follow the chronological order in which the blanks were run starting with the first FORM IV-HCIN and moving from left to right and continuing to the following FORM IV-HCIN as explained previously. 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.

6.13 Under "Comments", enter any ICB and CCB specific comments concerning the analyte results, any significant problems encountered during the ICB, CCB and PB analysis (i.e., blanks outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

7. <u>ICP Interference Check Sample</u> [FORM V - HCIN]

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

7.2 Complete the header information according to the header instructions and as follows.

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

7.4 For "ICS Source", enter the ICS source (12 characters maximum each), as previously explained in item 4.3. For EPA solutions, include the name and number identifying it (e.g., EPA-LV87). The laboratory must use the identification supplied by the EPA.

7.5 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

7.6 Under "TRUE Sol. A", enter the true concentration (in mg/L, to three decimal places) of each analyte present in Solution A.

7.7 Under "TRUE Sol. AB", enter the true concentration (in mg/L, to three decimal places) of each analyte present in Solution AB.

7.8 Under "INITIAL FOUND Sol. A", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the initial analysis of Solution A as required in Exhibit E.

7.9 Under "INITIAL FOUND Sol. AB", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the initial analysis of Solution AB as required in Exhibit E.

7.10 Under "INITIAL FOUND %R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-7:

$$\% R = \frac{\textit{Found Initial Solution AB}}{\textit{True Solution AB}} \times 100 \qquad \text{B-7}$$

7.11 Under "FINAL FOUND Sol. A", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the final analysis of Solution A as required in Exhibit E.

7.12 Under "FINAL FOUND Sol. AB", enter the found concentration (in mg/L, to three decimal places) of each analyte measured in the final analysis of Solution AB as required in Exhibit E.

7.13 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.

7.14 Under "FINAL FOUND %R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-8:

$$\% R = \frac{\textit{Found Final Solution AB}}{\textit{True Solution AB}} \times 100 \qquad \text{B-8}$$

NOTE: 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 eight-hour limit), it must be reported in the "FINAL FOUND" section of this form.

7.15 If more ICS analyses were required, submit additional copies of FORM V-HCIN as appropriate.

7.16 The order of reporting ICSs for each analyte must follow the temporal order in which the standards were run starting with the first FORM V-HCIN and continuing to the following FORM V-HCIN 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 in the same manner.

7.17 Under "Comments", enter any ICS specific comments concerning the analyte results, any significant problems encountered during the ICS analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

8. Spike Sample Recovery [FORM VI - HCIN]

8.1 This form is used to report results for the spike sample recovery which is based on the addition of a known quantity of analyte to the pre-digest sample.

8.2 Complete the header information according to the header instructions and as follows.

8.3 In the "EPA SAMPLE NO." box, enter the EPA Sample Number (10 characters maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box. Note that the EPA Sample No. must include the phase suffix and spike sample suffix for which the spike analyses are reported.

8.4 For "Phase", enter the phase identifier that describes the sample listed on this form.

8.5 For "Percent", enter the percent of the phase that constitutes the sample listed on this form.

NOTE: The entries for both "Phase" and "Percent" on this form must be identical to the entries made on FORM I-HCIN for the same sample.

8.6 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

8.7 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.

8.8 Under "SPIKED SAMPLE RESULT (SSR)", enter the concentration (in mg/Kg, to three decimal places) of each analyte in the spike sample. Enter any appropriate qualifier in the "C" qualifier column immediately following the Spiked Sample Result (SSR) column.

8.9 Under "SAMPLE RESULT (SR)", enter the concentration (in mg/Kg, to three decimal places) of each analyte measured in the sample (reported in the EPA Sample No. box) on which the matrix spike was performed. Enter any appropriate qualifier in the "C" qualifier column immediately following the Sample Result (SR) column.

8.10 Under "SPIKE ADDED (SA)", enter the concentration (in mg/Kg, to three decimal places) of each analyte added to the sample. If the "Spike Added" concentration is specified in the contract, the value added and reported must be that specific concentration in mg/Kg.

8.11 Under "% R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-9:

$$\% R = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{B-9}$$

NOTE: % R must be reported, whether it is negative, positive or zero. A value of zero must be used for SSR or SR if the analyte value is less than the MDL.

8.12 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).

8.13 Under "M", enter the method used or enter "NR" if the analyte is not required in the spike.

NOTE: If different samples (of the same phase) were used for spike sample analysis of different analytes, additional copies of FORM VI-HCIN must be submitted for each sample as appropriate.

8.14 Use additional copies of FORM VI-HCIN for each sample phase type on which a required spike sample analysis was performed.

8.15 Under "Comments", enter any spike sample specific comments concerning the analyte results, any significant problems encountered during the spike sample analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

9. Analytical Spike Sample Recovery [FORM VII - HCIN]

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

9.2 Complete the header information according to the header instructions and as follows.

9.3 For "Phase", enter the phase identifier that describes the sample listed on this form.

9.4 For "Percent", enter the percent of the phase that constitutes the sample listed on this form.

NOTE: The entries for both "Phase" and "Percent" on this form must be identical to the entries made on FORM I-HCIN for the same sample.

9.5 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to

the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

9.6 In the "EPA SAMPLE NO." box, enter the EPA Sample Number (10 characters maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box. Note that the EPA Sample No. must include the phase suffix and spike sample suffix for which the spike analyses are reported.

9.7 Under "CONTROL LIMIT %R" and "Q", the fields must be left blank until limits are established by the EPA. At that time, the Contractor will be informed on how to complete these fields.

9.8 Under "SPIKED SAMPLE RESULT (SSR)", enter the concentration (in mg/L, to three decimal places), for each analyte in the analytical spike sample. Enter any appropriate qualifier in the "C" qualifier column immediately following the spiked sample result (SSR) column.

9.9 Under "SAMPLE RESULT (SR)", enter the concentration (in mg/L, to three decimal places), for each analyte measured in the sample (reported in the EPA Sample No. box) on which the analytical spike was performed. Enter any appropriate qualifier in the "C" qualifier column.

9.10 Under "SPIKE ADDED (SA)", enter the concentration (in mg/L, to three decimal places) of each analyte added to the sample. If the spike added concentration is specified in the contract, the concentration added and reported must be that specific concentration in mg/L.

9.11 Under "% R", enter the value (to the nearest whole number) of the percent recovery for all spiked analytes computed according to equation B-10:

$$\% R = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{B-10}$$

9.12 Percent recovery must be reported, whether it is negative, positive, or zero.

9.13 A value of zero must be substituted for SSR or SR if the analyte concentration is less than the MDL.

9.14 Under "M", enter the method used or enter "NR" if the analyte is not required in the spike.

9.15 If different samples (of the same phase) were used for spike sample analysis of different analytes, additional copies of FORM VII-HCIN must be submitted for each sample as appropriate.

9.16 Use additional copies of FORM VII-HCIN for each sample phase type on which a required spike sample analysis was performed.

9.16 Under "Comments", enter any analytical spike sample specific comments concerning the analyte results, any significant problems encountered during the analytical spike sample analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

10. Duplicates [FORM VIII - HCIN]

10.1 This form is used to report results of duplicate analyses for determining the precision of the method.

10.2 Complete the header information according to the header instructions and as follows.

10.3 In the "EPA SAMPLE NO." box, enter the EPA Sample Number (10 characters maximum) of the sample from which the duplicate results on this form were obtained. The number must be centered in the box. NOTE: The EPA Sample No. must include the phase suffix and duplicate sample suffix for which the duplicate analyses are reported.

10.4 For "Phase", enter the phase description of the sample reported on this form.

10.5 For "Sample Percent", enter the percent of the phase that constitutes the sample reported on this form. Note that this percent must be identical to the entry made on FORM I-HCIN on which the initial analysis is made.

10.6 For "Duplicate Percent", enter the percent of the phase that constitutes the duplicate sample reported on this form.

10.7 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

10.8 Under "CONTROL LIMIT % R", enter the numerical value of the CRQL (in mg/Kg) for the analyte if the sample or duplicate values was less than five times CRQL. If the sample and duplicate values were less than the CRQL or greater than or equal to five times CRQL, leave the field empty.

10.9 Under "SAMPLE (S)", enter the concentration (in mg/Kg, to three decimal places) of each analyte in the original sample (reported in the EPA Sample No. box) on which a duplicate analysis was performed. Enter any appropriate qualifier in the "C" qualifier column immediately following the "SAMPLE (S)" column.

10.10 Under "DUPLICATE (D)", enter the concentration (in mg/Kg, to three decimal places) of each analyte measured in the duplicate sample (reported in the EPA Sample No. box). Enter any appropriate qualifier in the "C" qualifier column immediately following the "DUPLICATE (D)" column.

10.11 For all samples, the concentration of the original sample must be computed using the weight and "Sample Percent" of the original sample. The concentration of the duplicate sample must be computed using the weight and "Duplicate Percent" of the duplicate sample.

10.12 Under "RPD", enter the absolute value (to the nearest whole number) of the Relative Percent Difference for all analytes detected above the MDL in either the sample or the duplicate, computed according to equation B-11:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad \text{B-11}$$

10.13 A value of zero must be substituted for S or D if the analyte concentration is less than the MDL in either one. If the analyte concentration is less than the MDL in both S and D, leave the RPD field empty.

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

10.15 Under "M", enter the method used.

10.16 If different samples (of the same phase) were used for duplicate sample analysis of different analytes, then additional copies of FORM VIII-HCIN must be submitted for each sample as appropriate.

10.17 Use additional copies of FORM VIII-HCIN for each sample phase type on which a required duplicate sample analysis was performed.

10.18 Under "Comments", enter any duplicate sample specific comments concerning the analyte results, any significant problems encountered during the duplicate sample analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

11. Laboratory Control Sample [FORM IX - HCIN]

11.1 This form is used to report results for the specified High Concentration Laboratory Control Sample (LCS).

11.2 Complete the header information according to the header instructions and as follows.

11.3 For "ICP Source", enter the appropriate identifier (12 characters maximum) provided by the EPA for the LCS solution that was analyzed by ICP. The same criteria applies to the sources of the standards for the other methods such as HYICP, GFAA, cyanide and mercury.

11.4 If no analytes were analyzed by a certain method or if the analyte was not required to be analyzed, then leave the appropriate spaces empty.

11.5 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

11.6 Under "LIMITS", enter the lower limit (in mg/Kg. to the nearest whole number) in the left column, and the upper limit (in mg/Kg. to the nearest whole number) in the right column for each analyte in the High Concentration LCS.

11.7 Under "TRUE", enter the true concentration (in mg/Kg. to three decimal places) of each analyte in the High Concentration LCS.

11.8 Under "FOUND", enter the found concentration (in mg/Kg. to three decimal places) of each analyte measured in the High Concentration LCS.

11.9 Under "C", enter "B" or "U" or leave empty to describe the found value of the LCS.

11.10 Under "% R", enter the value (to the nearest whole number) of the percent recovery computed according to equation B-12:

$$\% R = \frac{Found\ LCS}{True\ LCS} \times 100 \qquad \text{B-12}$$

11.11 If the analyte concentration is less than the MDL, a value of zero must be substituted for the LCS Found.

11.12 Submit additional copies of FORM IX-HCIN as appropriate, if more than one LCS was required. In addition, submit additional copies of FORM IX-HCIN if more than one wavelength was used to determine an analyte for a sample phase type.

11.13 Under "Comments", enter any LCS specific comments concerning the analyte results, any significant problems encountered during the LCS analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

12. Standard Addition Results [FORM X - HCIN]

12.1 This form is used to report the results of samples analyzed using the Method of Standard Additions (MSA).

12.2 Complete the header information according to the header instructions and as follows.

12.3 Under "EPA SAMPLE NO.", enter the EPA Sample Numbers (10 characters maximum) of the analytical or field sample analyzed by MSA. The number must be centered in the box. Note that the EPA Sample No. must include the phase suffix and duplicate sample suffix (if applicable) of all analytical samples analyzed by MSA. This includes reruns by MSA (if the first MSA was out of control), as explained in Exhibits D and E.

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

12.5 Under "An", enter the chemical symbol (two characters maximum) for each analyte on which MSA was required for each sample reported. The analytes must be in an alphabetic listing of the chemical symbols.

12.6 Under "M", enter the method used.

NOTE: Results for different samples for each analyte must be reported sequentially, with the analytes listed 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.

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

12.8 Under "FIRST Added", enter the final concentration (in mg/L, to three decimal places) of the analyte (excluding sample contribution) after the first addition to the sample analyzed by MSA.

12.9 Under "FIRST Found", enter the measured value in absorbance units (to three decimal places) for the analyte in the sample solution spiked with the first addition.

12.10 Under "SECOND Added", enter the final concentration (in mg/L, to three decimal places) of the analyte (excluding sample contribution) after the second addition to the sample analyzed by MSA.

12.11 Under "SECOND Found", enter the measured value in absorbance units (to three decimal places) for the analyte in the sample solution spiked with the second addition.

12.12 Under "THIRD Added", enter the final concentration (in mg/L, to three decimal places) of the analyte (excluding sample contribution) after the third addition to the sample analyzed by MSA.

12.13 Under "THIRD Found", enter the measured value in absorbance units (to three decimal places) for the analyte in the sample solution spiked with the third addition.

NOTE: "ZERO Found", "FIRST Found", "SECOND Found", and "THIRD Found" must have the same dilution factor.

12.14 Under "FINAL CONC.", enter the final analyte concentration (in mg/L, to three decimal places) in the sample as determined by MSA according to equation B-13:

$$\textit{Final Conc.} = (-1) \times (\textit{x-intercept}) \qquad \text{B-13}$$

NOTE: The final concentration of an analyte does not have to equal the value for that analyte which is reported on FORM I-HCIN for that sample.

12.15 Under "r", enter the correlation coefficient (to three decimal places) that is obtained for the least squares regression line representing the following points (x,y):(0.0, "ZERO Found"), ("FIRST Added", "FIRST Found"), ("SECOND Added", "SECOND Found"), ("THIRD Added", "THIRD Found").

12.16 The correlation coefficient must be calculated using the ordinary least squares linear regression (unweighted) according to equation B-14:

$$r = \frac{N\,S\,xy_i - Sx_i\;\;Sy_i}{[\,N\,S\,x_i^2 - (\,S\,x_i\,)^2\,]^{1/2} \times [\,N\,S\,y_i^2 - (\,S\,y_i\,)^2\,]^{1/2}} \qquad \text{B-14}$$

12.17 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.

12.18 Under "Comments", enter any MSA specific comments concerning the analyte results, any significant problems encountered during the MSA analysis (i.e., percent recovery outside the control limits), both technical and administrative, the corrective action taken, and resolution performed for the sample.

13. Method Detection Limit [FORM XI - HCIN]

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

13.2 Complete the header information according to the header instructions and as follows.

13.3 For "DATE", enter the date (formatted MM/DD/YY) on which the MDL values were determined (or became effective).

13.4 Enter the instrument ID numbers for the fields "ICP ID Number", "HYICP ID Number", "GFAA ID Number", "Mercury ID Number", and "Cyanide ID Number" (12 characters maximum each). These ID Numbers are used to uniquely identify each instrument that the laboratory uses for CLP analyses.

13.5 Under "Wavelength", enter the wavelength in nanometers (to two decimal places) for each analyte for which a Method Detection Limit (MDL) has been established and is listed in the MDL column. If more than one wavelength is used for an analyte, use other copies of FORM XI-HCIN as appropriate to report the Method Detection Limit used, submit additional copies of FORM XII-HCIN as appropriate.

13.6 Under "WAVE", enter the wavelength number for which the results of each analyte are reported on the form. The wavelength number is a number assigned to each wavelength used when more than one wavelength is used to obtain data for an analyte in the SDG. A wavelength number of "1" is assigned to the longest wavelength used for the analyte in the SDG. A wavelength number of "2" is assigned to the second longest wavelength and so on. The field must be left blank if a single wavelength is used to obtain data for an analyte in the SDG.

13.7 Under "INTEG. TIME", enter the integration time (in seconds, to two decimal places) used for each measurement taken from each instrument.

13.8 The Contract Required Quantitation Limits (in mg/Kg), as established in Exhibit C, must appear in the column headed "CRQL".

13.9 Under "MDL", enter the Method Detection limit (in mg/L, to three decimal places) as determined by the laboratory for each analyte analyzed by the instrument for which the ID number is reported on this form.

13.10 Under "M", enter the method used to determine the method detection limit for each wavelength used.

13.11 Use additional copies of FORM XI-HCIN 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.

14. ICP Interelement Correction Factors (Annual) [FORM XII - HCIN]

14.1 This form documents for each ICP instrument the interelement correction factors applied by the Contractor laboratory to obtain data for the SDG.

14.2 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 XII-HCIN.

14.3 Complete the header information according to the header instructions and as follows.

14.4 For "ICP ID Number", enter the ICP ID Number (12 characters 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 copies of FORM XII-HCIN as appropriate.

14.5 For "Date", enter 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. Also, it must not precede them by more than twelve calendar months.

14.6 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 copies of FORM XII-HCIN as appropriate.

14.7 Under "INTERELEMENT CORRECTION FACTORS FOR:", enter the chemical symbol in the two space header field provided to indicate the analyte for which the corrections in that column were applied.

14.8 In the "INTERELEMENT CORRECTION FACTORS FOR:" column, enter the correction factor (negative, positive or zero, to seven decimal places, 10 characters maximum) for each corrected analyte analyzed by ICP. If an analyte was not corrected for an analyte that is listed in the header of a column, a zero must be entered to indicate that the correction was determined to be zero.

14.9 Use additional copies of FORM XII-HCIN as appropriate if correction factors for more than five analytes were applied.

14.10 Columns of correction factors for analytes requiring interelement correction must be entered left to right starting on FORM XII-HCIN according to the alphabetic order of their chemical symbols starting on the first FORM XII-HCIN and proceeding to the following FORM XII-HCIN as appropriate.

14.11 Under "Comments", enter alternative wavelengths and the conditions under which they are used, any significant problems encountered during the interelement correction analysis, both technical and administrative, the corrective action taken, and resolution performed for the sample.

15. Phase Separation Log [FORM XIII - HCIN]

15.1 This form is used to report the separation of the phases.

15.2 All samples that are phase separated in association with the SDG must be reported on a FORM XIII-HCIN. One (1) FORM XIII-HCIN must be submitted if no more than 32 phases were separated for the data deliverables required by the SDG. If more than 32 samples were separated, then submit additional copies of FORM XIII-HCIN as appropriate.

15.3 Complete the header information according to the header instructions and as follows.

15.4 For "Separation Date", enter the dates (formatted MM/DD/YY) on which the phase separation for the samples listed on the form were performed. If phase separation for the samples in the SDG were performed on different dates, submit additional copies of FORM XIII-HCIN for each date as appropriate.

15.5 Under "EPA SAMPLE NO.", enter the EPA Sample Number for each phase separated in the SDG. All EPA Sample Numbers must be listed in ascending alphanumeric order, continuing to the next FORM XIII-HCIN if applicable. If a sample consists of more than one phase, enter the EPA Sample Number in the order of increasing phase suffix.

15.6 Under "PHASE", enter the phase for each sample reported on the form.

15.7 Under "WATER MISCIBILITY", enter "YES" if the phase of the sample listed is water miscible, "NO" if the phase is non-water miscible, and "PART" if the phase is partially water miscible. If the sample phase is not liquid, then leave the field empty.

15.8 Under "WEIGHT", enter the weight (in grams, to two decimal places) of each phase reported on the form.

15.9 Under "PERCENT OF TOTAL SAMPLE", enter the percent of total sample (to two decimal places), that the phase reported constitutes of the total sample weight calculated according to equation B-15:

$$\%\ of\ Total\ Sample = \frac{Phase\ Weight\ in\ Grams}{Total\ Sample\ Weight\ in\ Grams} \times 100 \qquad \text{B-15}$$

15.10 Under "CENTRIFUGE TIME", enter the total centrifuge time (in minutes) for each phase listed.

16. Preparation Log [FORM XIV - HCIN]

16.1 This form is used to document the sample preparations.

16.2 All field samples (including all phases of each sample) and all quality control preparations (including duplicates, spikes, LCSs, PBs and reprepared samples) associated with the SDG must be reported on FORM XIV-HCIN. Only the preparations associated with the SDG may be submitted on this form.

16.3 Submit one FORM XV-HCIN per method if no more than 32 preparations, including quality control preparations, were performed. If more than 32 preparations per method were performed, then submit additional copies of FORM XV-HCIN as appropriate.

16.4 Complete the header information according to the header instructions and as follows.

16.5 For "Method", enter the method of analysis (2 characters maximum) for which the preparations listed on the form were made.

16.6 Under "EPA SAMPLE NO.", enter the EPA Sample Number (including phase suffix) of each sample in the SDG and of all other preparations, such as duplicates, spikes, LCSs, PBs, and repreparations (all formatted according to Table 1, Section II of this exhibit). All EPA Sample Numbers must be listed in ascending alphanumeric order, continuing to the next FORM XIV-HCIN if applicable. If a sample was reprepared, list the same EPA Sample Number in the order of increasing preparation date.

16.7 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.

16.8 Under "WEIGHT", enter the weight (in grams, to two decimal places) of each sample prepared for analysis by the method indicated in the header section of the form.

16.9 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.

16.10 Under "COLOR" and "CLARITY", enter the description of the sample after preparation in accordance with the descriptive terms used on FORM I-HCIN.

17. Analysis Run Log [FORM XV - HCIN]

17.1 This form is used to document the analysis sequence.

17.2 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 analyses following the last SOW-required field sample.

17.3 All field samples (including all phases of each sample) and all quality control preparations (including calibration standards, ICVs, CCVs, ICBs, CCBs, ICSs, LCSs, PBs, duplicates, pre-digestion

spikes, analytical spikes, and spike addition analyzed by the method of standard addition) associated with the SDG must be reported on FORM XV-HCIN. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

17.4 Submit one FORM XV-HCIN per run if no more than 32 analyses, including instrument calibration, were analyzed in the run. If more than 32 analyses were performed in the run, submit additional copies of FORM XV-HCIN as appropriate.

17.5 Complete the header information according to the header instructions and as follows.

17.6 For "Instrument ID Number", enter the instrument ID number (12 characters maximum) which is the identifier that distinguishes each instrument used for analysis in the SDG. If more than one instrument is used, submit additional copies of FORM XV-HCIN as appropriate.

17.7 For "Method", enter the method code (two characters maximum).

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

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

17.10 Under "EPA SAMPLE NO.", enter the EPA Sample Number, including phase and QC suffix of each sample (formatted according to Table 1, Section II of this Exhibit). All EPA Sample Numbers must be listed in increasing temporal (date and time) order of analysis, continuing to the next FORM XV-HCIN 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 "ZZZZZ".

17.11 Under "D/F", enter the dilution factor (to three decimal places) by which the final product of the preparation procedure (digestate or distillate) can be analyzed within the instrument standard range. The dilution factor does not include the dilution inherent in the preparation as specified by the preparation procedures in Exhibit D. NOTE: A "1" must be entered if the preparation product was analyzed without adding any further volume of dilutant or any other solutions to the "Volume" or an aliquot of the "Volume" listed on FORM XV-HCIN for that sample.

17.12 For EPA supplied solutions such as ICVs, ICSs, and LCSs, a dilution factor must be entered if the supplied solution was used at 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, the ICV-2(0887) has a true value of 104.0 μg/L for selenium 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 XV-HCIN and the uncorrected instrument reading is compared to a true value of 52 μg/L. In this example, FORM II-HCIN 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 XV-HCIN using equation B-16:

$$\textit{Found Value on Form II-HCIN} = \textit{Instrument Readout in mg/L} \times D/F \qquad \text{B-16}$$

17.13 Under "TIME", enter the time (in military format - HHMM), at which each analysis was performed. If an autosampler is used with equal analysis time and intervals between analyses, then only the start time of the run (the time of analysis of the final CCV or CCB, whichever is later) needs to be reported.

17.14 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.

18. Sample Log-in Sheet [FORM HDC-1]

18.1 This form is used to document the receipt and inspection of shipping containers and samples. One (1) original FORM HDC-1 is required for each shipping container.

18.2 If the samples in a single shipping container must be assigned to more than one SDG, then the original FORM HDC-1 shall be placed with the deliverables for the SDG of the lowest alphanumeric number and a copy of FORM HDC-1 must be placed with the deliverables for the other SDG(s). The copies should be identified as "copy(ies)," and the location of the original should be noted on the copies.

18.3 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 one on FORM HDC-1. Record the custody seal numbers in item two.

18.4 Open the shipping container, remove the enclosed sample documentation, and record on FORM HDC-1, items three-five, the presence/absence of chain-of-custody record(s), SMO forms (i.e., Traffic Reports, Packing Lists), and airbills or airbill stickers. Specify if there is an airbill or an airbill sticker present in item five on FORM HDC-1. Record the airbill or sticker number in item six.

18.5 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 the presence or absence of sample tags in items seven and eight on FORM HDC-1.

18.6 Review the sample shipping documents and complete the header information. Compare the information recorded on all the documents and samples, and circle the appropriate answer in item nine on FORM HDC-1.

18.7 If there are no problems observed during receipt, sign and date (include time) FORM HDC-1, the chain-of-custody record, and TR, and write the sample numbers on FORM HDC-1. Record the appropriate sample tags and assigned laboratory numbers if applicable. The log-in date should be recorded at the top of FORM HDC-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.

18.8 If there are problems observed during receipt or if an answer marked with an asterisk (i.e., "absent*") was circled, then contact SMO and document the 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.

18.9 For "Sample Transfer", enter 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 HDC-1. Sign and date the sample transfer block.

19. Document Inventory Sheet [FORM HDC-2]

19.1 This form is used to record the inventory of the Complete Sample Delivery Group Case file (CSF) documents which are sent to the Region.

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

19.3 Certain laboratory specific documents related to the CSF may not fit into a clearly defined category. The laboratory should review FORM HDC-2 to determine if it is most appropriate to place them under No. 28, 29, 30, or 31. Category 31 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.

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION IV

DATA REPORTING FORMS

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

COVER PAGE

Lab Name: _____ Contract: _____

Lab Code: _____ SAS No.: _____

Case No.: _____ SDG No.: _____

SOW No.: _____

EPA Sample No.	Lab Sample ID

	Enter "Y" for Yes or "N" for No
ICP interelement corrections applied?	_____
ICP background corrections applied?	_____
If yes, were raw data generated before application of background corrections?	_____

Comments: _____

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

Signature: _____ Name: _____

Date: _____ Title: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

EPA SAMPLE NO

ANALYSIS DATA SHEET

Lab Name: _____ Contract: _____
Lab Code: _____ Lab Sample ID: _____
Case No.: _____ Date Received: _____
SAS No.: _____ Phase: _____
SDG No.: _____ Percent: _____
Water Miscibility: _____ Color: _____
Texture: _____ Clarity: _____
Artifacts: _____ Viscosity: _____

pH: _____ Concentration Units: mg/Kg Conductivity: _____

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				
7882-49-2	Selenium				
7440-22-4	Silver				
7440-23-5	Sodium				
7440-28-0	Thallium				
7440-62-2	Vanadium				
7440-66-6	Zinc				
	Cyanide				

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: _____ Contract: _____

Lab Code: _____ Initial Calibration Source: _____

Case No.: _____ Continuing Calibration Source: _____

SAS No.: _____ Concentration Units: mg/L

SDG No.: _____

ANALYTE	WAVE	INITIAL CALIBRATION			CONTINUING CALIBRATION						M
					FIRST			SECOND			
		True	Found	%R	True	Found	%R	True	Found	%R	
Aluminum											
Antimony											
Arsenic											
Barium											
Beryllium											
Cadmium											
Calcium											
Chromium											
Cobalt											
Copper											
Iron											
Lead											
Magnesium											
Manganese											
Mercury											
Nickel											
Selenium											
Silver											
Sodium											
Thallium											
Vanadium											
Zinc											
Cyanide											

Comments:

_____

_____

_____

_____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

CRQL STANDARDS / LINEAR RANGE STANDARDS

Lab Name: _____ Contract: _____

Lab Code: _____ SAS No.: _____

Case No.: _____ SDG No.: _____

CRQL:
- ICP Source: _____
- HYICP Source: _____
- GFAA Source: _____
- Cyanide Source: _____
- Mercury Source: _____

LRS:
- ICP Source: _____
- ICP Date: _____
- HYICP Source: _____
- HYICP Date: _____

Concentration Units: mg/L

ANALYTE	WAVE	CRQL STANDARDS						LINEAR RANGE STANDARDS			
		INITIAL			FINAL						
		True	Found	%R	Found	%R	M	True	Found	%R	M
Aluminum											
Antimony											
Arsenic											
Barium											
eryllium											
Cadmium											
Calcium											
Chromium											
Cobalt											
Copper											
Iron											
Lead											
Magnesium											
Manganese											
Mercury											
Nickel											
Selenium											
Silver											
Sodium											
Thallium											
Vanadium											
Zinc											
Cyanide											

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

BLANKS

Lab Name: _____ Contract: _____

Lab Code: _____ SDG No.: _____

Case No.: _____ Preparation Blank Phase: _____

SAS No.: _____ Concentration Units: mg/L

ANALYTE	WAVE	INITIAL CALIB. BLANK		CONTINUING CALIBRATION BLANK							PREPARATION BLANK		
			C	1	C	2	C	3	C		mg/Kg	C	M
Aluminum													
Antimony													
Arsenic													
Barium													
Beryllium													
Cadmium													
Calcium													
Chromium													
Cobalt													
Copper													
Iron													
Lead													
Magnesium													
Manganese													
Mercury													
Nickel													
Selenium													
Silver													
Sodium													
Thallium													
Vanadium													
Zinc													
Cyanide													
pH	NA												
Conductivity	NA												

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

ICP INTERFERENCE CHECK SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ ICP ID No.: _____

Case No.: _____ ICS Source: _____

SAS No.: _____ Concentration Units: mg/L

SDG No.: _____

ANALYTE	WAVE	TRUE		INITIAL FOUND			FINAL FOUND			
		Sol. A	Sol. AB	Sol. A	Sol. AB	%R	Sol. A	Sol. AB	%R	M
Aluminum										
Antimony										
Arsenic										
Barium										
Beryllium										
Cadmium										
Calcium										
Chromium										
Cobalt										
Copper										
Iron										
Lead										
Magnesium										
Manganese										
Mercury										
Nickel										
Selenium										
Silver										
Sodium										
Thallium										
Vanadium										
Zinc										

Comments:

_____

_____

_____

_____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Phase: _____

Case No.: _____ Percent: _____

SAS No.: _____ Concentration Units: mg/Kg

SDG No.: _____

ANALYTE	WAVE	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										
Selenium										
Silver										
Sodium										
Thallium										
Vanadium										
Zinc										
Cyanide										

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

EPA SAMPLE NO

ANALYTICAL SPIKE SAMPLE RECOVERY

Lab Name: _____ Contract: _____

Lab Code: _____ Phase: _____

Case No.: _____ Percent: _____

SAS No.: _____ Concentration Units: mg/L

SDG No.: _____

ANALYTE	WAVE	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										
Selenium										
Silver										
Sodium										
Thallium										
Vanadium										
Zinc										
Cyanide										

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

DUPLICATES

EPA SAMPLE NO

Lab Name: _____ Contract: _____

Lab Code: _____ Phase: _____

Case No.: _____ Sample Percent: _____

SAS No.: _____ Duplicate Percent: _____

SDG No.: _____ Concentration Units: mg/Kg

ANALYTE	WAVE	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									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

LABORATORY CONTROL SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ SAS No.: _____

Case No.: _____ SDG No.: _____

ICP Source: _____ Cyanide Source: _____

HYICP Source: _____ Mercury Source: _____

GFAA Source: _____ Concentration Units: mg/Kg

ANALYTE	WAVE	LIMITS		TRUE	FOUND	C	%R	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide	NA							
pH	NA							NA
Conductivity	NA							NA

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

STANDARD ADDITION RESULTS

Lab Name: _____ Contract: _____

Lab Code: _____ SDG No.: _____

Case No.: _____ Concentration Units: mg/L

	EPA SAMPLE NO.	An	M	ADDITIONS							FINAL CONC.	r	Q
				ZERO	FIRST		SECOND		THIRD				
				Found	Added	Found	Added	Found	Added	Found			
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15													
16													
17													
18													
19													
20													
21													
22													
23													
24													
25													
26													
27													
28													
29													
30													
31													
32													

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

METHOD DETECTION LIMIT

Lab Name: _____ Contract: _____

Lab Code: _____ ICP ID Number: _____

Case No.: _____ HYICP ID Number: _____

SAS No.: _____ GFAA ID Number: _____

SDG No.: _____ Cyanide ID Number: _____

Date: _____ Mercury ID Number: _____

Concentration Units: mg/L

ANALYTE	WAVE-LENGTH (nm)	WAVE	INTEG. TIME (SEC)	CRQL (mg/Kg)	MDL	M
Aluminum				80		
Antimony				20		
Arsenic				10		
Barium				80		
Beryllium				10		
Cadmium				10		
Calcium				80		
Chromium				10		
Cobalt				20		
Copper				40		
Iron				20		
Lead				50		
Magnesium				80		
Manganese				10		
Mercury				0.3		
Nickel				20		
Selenium				10		
Silver				10		
Sodium				80		
Thallium				100		
Vanadium				20		
Zinc				10		
Cyanide				1.5		

Comments:

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

ICP INTERELEMENT CORRECTION FACTORS (ANNUAL)

Lab Name: _____ Contract: _____

Lab Code: _____ ICP ID Number: _____

Case No.: _____ Date: _____

SDG No.: _____

ANALYTE	WAVE-LENGTH (nm)	INTERELEMENT CORRECTION FACTORS FOR: -----	-----	-----	-----	-----
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Cyanide						

Comments: _____

U. S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

PHASE SEPARATION LOG

Lab Name: _____ Contract: _____

Lab Code: _____ SDG No.: _____

Case No.: _____ Separation Date: _____

	EPA SAMPLE NO.	PHASE	WATER MISCIBILITY	WEIGHT (grams)	PERCENT OF TOTAL SAMPLE	CENTRIFUGE TIME
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						

U.S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

PREPARATION LOG

Lab Name: _____ Contract: _____

Lab Code: _____ SDG No.: _____

Case No.: _____ Method: _____

	EPA SAMPLE NO.	PREPARATION DATE	WEIGHT (grams)	VOLUME	COLOR	CLARITY
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						

U.S. ENVIRONMENTAL PROTECTION AGENCY
CONTRACT LABORATORY PROGRAM
High Concentration Inorganics

ANALYSIS RUN LOG

Lab Name: _____ Contract: _____

Lab Code: _____ SDG No.: _____

Case No.: _____ SAS No.: _____

Start Date: _____ Method: _____

End Date: _____ Instrument ID Number: _____

	EPA SAMPLE NO.	TIME	D/F	ANALYTES																						
				AL	SB	AS	BA	BE	CD	CA	CR	CO	CU	FE	PB	MG	MN	HG	NI	SE	AG	NA	TL	V	ZN	CN
1																										
2																										
3																										
4																										
5																										
6																										
7																										
8																										
9																										
10																										
11																										
12																										
13																										
14																										
15																										
16																										
17																										
18																										
19																										
20																										
21																										
22																										
23																										
24																										
25																										
26																										
27																										
28																										
29																										
30																										
31																										
32																										

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: _____

CIRCLE THE APPROPRIATE RESPONSE:

1. Custody Seal(s) Present/Absent*
   Intact/Broken
2. Custody Seal Nos.: _____
   _____
3. Chain-of-Custody Records Present/Absent*
4. Traffic Reports or Packing List 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, an sample tags agree. Yes/No*
10. Date Received at Lab: _____
11. Time Received: _____

Sample Transfer

Fraction: _____ _____

Area #: _____ _____

By: _____ _____

On: _____ _____

EPA SAMPLE #	SAMPLE TAG #	ASSIGNED LAB #	REMARKS: CONDITION OF SAMPLE SHIPMENT ETC.

HIGH CONCENTRATION INORGANIC ANALYTES
COMPLETE SDG FILE (CSF)
INVENTORY SHEET

Lab Name: _____ City/State: _____

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

SAS No.: _____ Contract No.: _____ SOW No.: _____ IFB No.: _____

All documents delivered in the complete SDG file must be original documents where possible.
(Reference Exhibit B, Section III)

	Page Nos.		(Please Check:)	
	From	To	Lab	Region
1. Inventory Sheet (HDC-2) (Do not number)				
2. Cover Page				
3. Inorganic Analysis Data Sheet (FORM I-HCIN)				
4. Initial & Continuing Calibration Verification (FORM II-HCIN)				
5. CRQL Standards/Linear Range Standards (FORM III-HCIN)				
6. Blanks (FORM IV-HCIN)				
7. ICP Interference Check Sample (FORM V-HCIN)				
8. Spike Sample Recovery (FORM VI-HCIN)				
9. Analytical Spike Sample Recovery (FORM VII-HCIN)				
10. Duplicates (FORM VIII-HCIN)				
11. Laboratory Control Sample (FORM IX-HCIN)				
12. Standard Addition Results (FORM X-HCIN)				
13. Method Detection Limit (FORM XI-HCIN)				
14. ICP Interelement Correction Factors (Annual) (FORM XII-HCIN)				
15. Phase Separation Log (FORM XIII-HCIN)				
16. Preparation Log (FORM XIV-HCIN)				
17. Analysis Run Log (FORM XV-HCIN)				
18. ICP Raw Data				
19. HYICP Raw Data				
20. Graphite Furnace AA Raw Data				
21. Mercury Raw Data				
22. Cyanide Raw Data				
23. pH Raw Data				
24. Conductivity Raw Data				
25. Traffic Report				

	Page Nos.		(Please Check)	
	From	To	Lab	Region
26. EPA Shipping/Receiving Documents				
Airbill (No. of Shipments _____)	____	____	____	____
Chain-of-custody Records	____	____	____	____
Sample Tags	____	____	____	____
Sample Log-In Sheet (Lab & HDC-1)	____	____	____	____
SDG Cover Sheet	____	____	____	____
27. Misc. Shipping/Receiving Records (list all individual records)				
Telephone Logs	____	____	____	____
_____	____	____	____	____
_____	____	____	____	____
28. Internal Lab Sample Transfer Records & Tracking Sheets (describe or list)	____	____	____	____
29. Internal Originial Sample Preparation & Analysis Records (describe or list)				
Preparation Records _____	____	____	____	____
Analysis Records _____	____	____	____	____
Description _____	____	____	____	____
30. Other Records (describe or list)				
Telephone Communication Log	____	____	____	____
_____	____	____	____	____
_____	____	____	____	____

31. Comments:

_____

_____

Completed by (CLP Lab):

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

Audited by (EPA):

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

EXHIBIT C

INORGANIC ANALYTE TABLES

TABLE 1.

HIGH CONCENTRATION INORGANIC
TARGET ANALYTE LIST (TAL)

Analyte	Contract Required Quantitation Limit[1,2] (mg/Kg)
Aluminum	80
Antimony	20
Arsenic	10
Barium	80
Beryllium	10
Cadmium	10
Calcium	80
Chromium	10
Cobalt	20
Copper	40
Iron	20
Lead	50
Magnesium	80
Manganese	10
Mercury	0.3
Nickel	20
Selenium	10
Silver	10
Sodium	80
Thallium	100
Vanadium	20
Zinc	10
Cyanide	1.5
Conductivity	3.0 (μmhos/cm)
pH	NA

(1) The analytical methods specified in SOW Exhibit D must be utilized and the achieved method detection limits must meet the Contract Required Quantitation Limits (CRQL) requirements. Higher detection levels may only be used in the following circumstance:

If the sample concentration exceeds two 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 quantitation limit. The method detection limit must be documented as described in Exhibits D and E.

(2) These CRQLs are the method detection limits (for metals) and the maximum allowable method blank values (for all other parameters) obtained from actual method blank preparations that must be met using the procedure in Exhibits D and E.

TABLE 2.

INTERFERENCE CHECK SAMPLE

Solution A Elements	(mg/L)	Solution AB Interferents	(mg/L)
Ag	1.0	Al	500.
Ba	0.5	Ca	500
Be	0.5	Fe	500.
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		

TABLE 3.

INITIAL AND CONTINUING CALIBRATION VERIFICATION
CRQL STANDARD CONTROL LIMITS, AND LCS STANDARD CONTROL LIMITS
FOR INORGANIC ANALYSES

INITIAL AND CONTINUING CALIBRATION VERIFICATION LIMITS

Analytical Method	Inorganic Species	% of True Value (EPA Set) Low Limit	High Limit
ICP	Metals	90	110
HYICP	Metals	85	115
GFAA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other:	Cyanide	85	115

CRQL STANDARD CONTROL LIMITS

Analytical Method	Inorganic Species	% of True Value (EPA Set) Low Limit	High Limit
ICP	Metals	75	125
HYICP	Metals	75	125
GFAA	Metals	75	125
Cold Vapor AA	Mercury	75	125
Other:	Cyanide	75	125

LCS STANDARD CONTROL LIMITS

The LCS Standard Control Limits are the same for all inorganics species. The limits are 80 - 120 percent.

TABLE 4.

SPIKING LEVELS AND FORMS OF ANALYTE IN THE SOLID SPIKING MIXTURE

Analyte	Form	Spike Level (mg/Kg)
Antimony	SbO	1600
Arsenic	AsO	1600
Beryllium	$Be(C_2H_3O_2)_2$	1600
Cadmium	CdO	1600
Chromium	CrO	1600
Cobalt	$CoCO_3$	1600
Copper	CuO	1600
Lead	PbO	1600
Manganese	MnO	1600
Nickel	NiO	1600
Selenium	SeO	1600
Silver	AgO	1600
Thallium	TlO	1600
Vanadium	VO	1600
Zinc	ZnO	1600

NOTE: The spike concentration in solution after the potassium hydroxide fusion will be 4.0 mg/L.

TABLE 5.

LCS CONCENTRATION

Analyte	Concentration (mg/Kg)
Aluminum	2870
Antimony	164
Arsenic	1954
Barium	10
Beryllium	91
Cadmium	194
Calcium	76505
Chromium	315
Cobalt	346
Copper	8727
Iron	89020
Lead	86650
Magnesium	41318
Manganese	184
Mercury	2
Nickel	413
Potassium	160
Selenium	91
Silver	94
Sodium	359
Thallium	91
Vanadium	23647
Zinc	36764

EXHIBIT D

PREPARATION AND ANALYSIS METHODS

EXHIBIT D

TABLE OF CONTENTS

Page

SECTION I INTRODUCTION 83

Figure 1 High Concentration Inorganic Methods Flow Chart 84

SECTION II HOLDING TIMES AND STORAGE REQUIREMENTS 85

SECTION III METHODOLOGY AND DATA USER GUIDE 87

SECTION IV SAMPLE PREPARATION

Phase Separation and Aliquoting (Method 50.60-CLP) 91

SECTION V SAMPLE ANALYSIS

Potentiometric and Colorimetric Determination of the pH of Industrial Waste Materials (Method 150.20-CLP) 95

Determination of Conductivity in Industrial Waste Material (Method 120.1-CLP) 103

Dissolution of Industrial Waste Materials for Elemental Analysis by Potassium Hydroxide Fusion (Method 200.62-A-CLP) 109

Pneumatic Nebulization Inductively Coupled Argon Plasma Optical Emission Spectroscopic (ICP) Analysis (Method 200.62-B-CLP) 113

Hydride Generation Inductively Coupled Argon Plasma Optical Emission Spectroscopic (HYICP) Analysis (Method 200.62-C-CLP) 137

Determination of Potassium Hydroxide Fusion Samples by Graphite Furnace Atomic Absorption (GFAA) Technique 159

Atomic Absorption Spectroscopic Determination of Mercury in Industrial Waste Materials (CVAA) (Method 202.62-CLP) 179

Colorimetric Determination of Cyanide in Industrial Waste Materials (Method 335.63-CLP) 197

SECTION I

INTRODUCTION

The analytical scheme that the Contractor will follow in performing sample analyses under this contract is outlined in Figure 1, the High Concentration Inorganics Methods Flow Chart.

All analytical methods specified in Exhibit D may be utilized as long as the documented method quantitation limits meet the CRQLs listed in Exhibit C.

All samples shall be carried through the sample preparation procedure and then run undiluted. When an analyte concentration exceeds the calibrated or linear range, reanalysis of the prepared sample is required after appropriate dilution. For the sample dilution, the Contractors must use the lowest dilution factor necessary to bring each analyte within the valid analytical range and report the highest valid value for each analyte. Both diluted and undiluted sample measurements must be contained in the raw data.

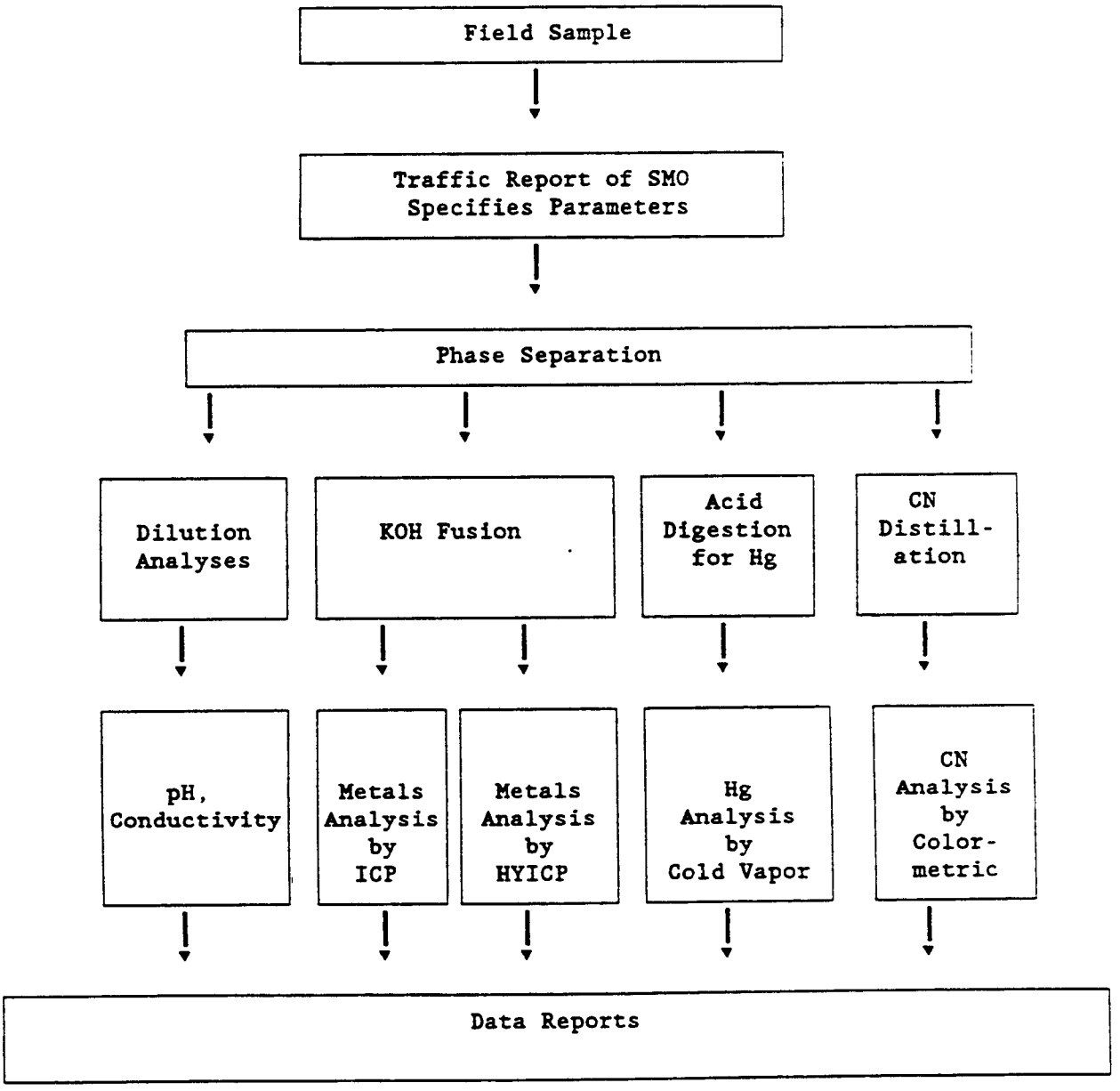
Samples must be opened and digested in a hood. Stock solutions for standards may be purchased or made up as specified in the analytical methods. All sample dilutions shall be made with acidified water to maintain constant acid strength. Unless otherwise instructed by the EPA APO or TPO, all samples must be mixed thoroughly prior to aliquoting for digestion.

For all ICP measurements, use the average intensity of multiple exposures for both standardization and all other analyses. A minimum of two replicate exposures are required. All standards with analyte concentrations made up of less than 1 mg/L are low level standards.

For HYICP, GFAA, and CVAA systems, calibration standards are prepared by diluting the stock metal solutions. Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. The date and time of preparation and analysis shall be given in the raw data.

FIGURE 1

High Concentration Inorganic Methods Flow Chart



SECTION II

HOLDING TIMES AND STORAGE REQUIREMENTS

1. Holding times

Under this contract, the following are the maximum sample holding times allowable. These holding time supersede any contract required delivery schedule.

Analyte	No. of Days Following Sample Receipt by Contractor
Mercury	26 days
Metals (other than Mercury)	180 days
Cyanide	12 days
pH	24 hours
Conductivity	24 hours

2. Storage requirements

The samples shall be stored in either glass or plastic polyethylene bottles in a secure location.

For liquid samples, the sample custodian shall store the material in an refrigerator at 4 ± 2°C.

For solid samples, the sample custodian shall store the material in an designated area in which to avoid possible contamination and endangerment to the health and safety of the employees.

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION III

METHODOLOGY AND DATA USER GUIDE

1. Scope

1.1 Samples of industrial waste materials gathered in support of EPA investigations of disposal, handling and storage practices are subjected to limited chemical characterization using the procedures and methods prescribed herein. This characterization is not designed to define the total composition of the samples, but is designed essentially to look for specific constituents. The characterization is targeted to the analysis of the priority pollutants and additional inorganic parameters.

1.2 Samples may be obtained from drummed materials, waste pits or lagoons, piles of waste, tanker trucks, onsite tanks, or apparent contaminated soil areas.

1.3 The waste materials usually are industrial process waste, byproducts, raw materials, intermediates and contaminated products. Many of the samples may be spent oil, spent solvents, paint wastes, metal treatment wastes, and polymer formulations.

1.4 The methods are included for the determination of 22 metals, cyanide, conductivity, and pH. Also included is a phase separation method that is applied to samples prior to digestion and analysis. Each individual phase is digested and analyzed by the specific methods. (A phase being either water miscible, non-water miscible, or solid.)

2. Limitations

2.1 A detailed knowledge of the chemical and physical properties of samples submitted for analysis, as well as the behavior of analytes under specific conditions, are not available with the wide variety of materials that are submitted under this contract. Although the analytical methods contained herein have been shown to be quantitative for a large number of sample matrices, the unknown nature of the samples prior to characterization can cause problems in certain instances.

2.2 The elemental constituent analysis approach only analyzes 22 metals. Interferences from metals not included in this analysis which may cause either positive or negative biases will not be corrected by this approach. The recovery of certain metals from a sample matrix may be affected by the presence of other metals or by the form of the metal, which may not be readily detected.

3. Characterization

3.1 Corrosivity of a waste may be determined by testing for either pH or rate of steel corrosion. The pH of water extracted samples as determined herein does not classify a waste as a RCRA waste but instead is determined for informative purposes such as to aid in waste segregation.

3.2 Reactive wastes may be wastes from one of many groups including unstable materials (explosives), materials that undergo violent reactions with water (sodium metal) or without water (pyrophorics), and materials that generate toxic vapors/gases upon reaction with water (phosphides) or mildly acidic conditions (cyanide). The methods for cyanide included here are "total" methods for cyanide amenable to distillation under strongly acidic conditions.

3.3 The identification of metal constituents, including priority pollutants, is part of the EPA determination of a toxic waste. This material is not a "toxic" waste in the normal usage of the word but is instead based on the potential for the hazardous constituents of the waste to leak out of the waste site (landfill, pond, etc.) and contaminate the soil and/or ground water.

4. Summary of Methodology

4.1 Phase separation is performed on the samples in an effort to improve both precision and accuracy. Precision is improved because once the sample is separated using standard protocols, the individual phases may be weighed and aliquoted without subjective decision making on the part of the technician as to what percentage of the sample each phase represents. Separation also improves precision in cases where different technicians may make an additional or repeat aliquots. Accuracy is improved with phase separation because by phase separating the sample, all phases are accounted for and included in the total sample concentration. Even if there is insufficient phase to aliquot all preparations, the examination of the separated phase will enable a more educated decision to be made as to which analysis is most appropriate. Also, obvious artifacts (see Method 50.60-CLP) can be more easily identified and eliminated from the analytical scheme.

4.2 The pH is determined by the use of a low sodium glass combination pH electrode or by an indicator test strip (colorimetric method).

4.3 The conductivity of a diluted or an undiluted sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent. The results of direct analyses of water miscible liquids are preferable to be analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C. The results of measuring for conductivity can aid in estimating sample size to be used for common chemical determinations, check results of a chemical analysis, estimate total filtrable residue in a sample, and measure the corrosion rate.

4.4 The potassium hydroxide fusion technique is used to dissolve inorganic metals from a wide variety of industrial waste materials. In particular, organic matter is largely destroyed and silica matrices are dissolved. This procedure takes an aliquot of sample and fuses it with 2 g of potassium hydroxide in a pyrolytically-coated graphite crucible. The mixture is then carried through various heating stages, cooled, rinsed with acid, mixed with hydrogen peroxide, and allowed to mix overnight to aid in dissolution and to outgas the peroxide.

4.5 The analytical methods provided for the determinations of the 22 metals and cyanide include ICP, HYICP, GFAA, CVAA, and colorimetric techniques.

5. Required Quantitation Limits

5.1 The required quantitation limits can be found in Exhibit C, Table 1.

6. Documentation and Reporting Forms

6.1 All raw analysis data including calibration and analysis printouts, associated notebook entries and laboratory bench and calculation sheets must be clearly labeled. Reanalysis of samples must be documented and clear identification of the various analytical runs must be present with the required submission of raw data. Reporting forms are found in Exhibit B.

7. Glassware Cleaning for Metals Determination

7.1 For the determination of metals in high concentration, high hazard samples, the problem of sample carry-over is a prime concern. Since the levels of metals in individual samples may vary significantly, all glassware should be treated on a worst-case basis. The following protocol must be used for glassware cleaning:

- Prior to removal from the hood, wash all glassware with hot, soapy water followed by a tap water rinse. Remove any remaining sample with the use of organic solvents followed by a hot, soapy wash and tap water rinse;
- Thoroughly rinse the glassware with 50 percent nitric acid;
- Thoroughly rinse with tap water;
- Thoroughly rinse with 50 percent hydrochloric acid;
- Thoroughly rinse with tap water;
- Soak the glassware for 24 hours in 25 percent nitric acid; and
- Rinse all glassware with sufficient ASTM Type I water (at lease three rinses) to remove all traces of acid.

NOTE: Chromic acid may be useful to remove organic deposits from glassware; however, the glassware must be thoroughly rinsed with water to remove the last traces of chromium. The glassware must be carried through the entire glassware cleaning protocol after the use of chromic acid.

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION IV

SAMPLE PREPARATION

Method 50.60-CLP

Phase Separation and Aliquoting

1. Scope and Application

1.1 This is a general purpose method that provides procedures for phase separating industrial waste samples taken from drums, lagoons, tanks, landfills, and other uncontrolled hazardous waste sites.

2. Summary of Method

2.1 Individual phases are separated by decanting and centrifuging. After separation, individual phases are measured to meet the total weight specified in the individual methods.

2.2 Phase separation is performed in order to obtain representative aliquots from the original sample and to characterize the different phases present in the sample.

3. Sample Characteristics

3.1 The characteristics of the samples defined below are the only descriptions to be used in describing the physical attributes of the samples (specific comments may be used when appropriate):

- Phase — A solid (gel or paste) or liquid (water miscible or non-water miscible);
- Paste — Inseparable solid and liquid;
- Viscosity — Nonviscous (similar to water) or viscous;
- Color — Colorless, light, medium or dark in color. Use only primary and secondary colors - red, blue, yellow, green, violet, orange, brown, white, gray, or black;
- Texture — Fine (powdery), medium (sand) or coarse (large crystals or rocks);
- Clarity — Clear, cloudy (transmits light) or opaque; and
- Minor Phase — Phases that represent less than or equal to 1 percent by weight of the total sample.

4. Artifacts

4.1 Artifacts may occur in the sample depending on the nature of the waste and how it was obtained. Artifacts are not minor phases but are due to extraneous agents not of the waste. When excluding a portion of a sample from aliquoting based on the apparent presence of an artifact, the decision should be fully documented on the cover page.

5. Apparatus and Equipment

5.1 Centrifuge, explosion-proof:

- Large process type for 8 oz. jars; and
- Small type for vials.

5.2 Vials and jars with teflon lined caps:

- 2 dram vials;
- 40 mL vials;
- 20 mL vials;
- 8 oz. jars; and
- 4 oz. jars.

5.3 Pipets, various sizes.

5.4 Balance, four place.

5.5 Spatulas, various types.

5.6 Miscellaneous:

- Absorbent toweling;
- Soap and water squirt bottles;
- Solvent squirt bottles (methanol, acetone, methylene chloride);
- Plastic bags, various sizes;
- Stainless steel trays; and
- Teflon cap liners, various sizes.

6. Procedure

6.1 Place the sample can inside a plastic trash bag. Remove the sample container(s) from the can and record the type and number of containers present. Wipe down the sample container(s) with a towel moistened with soapy water.

6.2 Record any other sample information present.

6.3 **Phase Separation**

6.3.1 If the sample is multi-phase, split the sample into two jars, place the jars in plastic bags and centrifuge them at 3000 rpm. Centrifuge the sample containers for not less than five minutes but no longer than ten minutes. Check for separation completeness. If incomplete, centrifuge for an additional five minutes. Record the total centrifugation time.

6.3.2 Transfer each individual phase to an appropriate tared and labeled vial or jar and record the individual phase weights, the phase weight percentages and the total sample weight for each phase

6.3.3 For each liquid phase, test for water miscibility by adding several drops of sample to a 2 dram vial containing 0.5 mL of ASTM Type II water. Record the results as water miscible, partially water miscible or non-water miscible. Transfer 35 mL of the liquid to a labeled 40 mL vial or 2 oz. bottle. Recap original sample.

6.3.4 For each solid or paste phase, transfer approximately 35 g into a labeled container.

6.4 Record description of each phase on the phase log form using phase descriptions described in Exhibit B.

6.5 Remove any material from the outside of vials and jars with toweling and soap and water. (Solvents may be necessary, but use only on sealed containers.) Place container, separated phases into one plastic autoclave bag and store for future aliquoting.

6.6 Aliquoting

6.6.1 Weigh a predetermined amount of each phase into an appropriate test vial and record the weight of each phase. Refer to individual methods for specific weights.

6.6.2 Unless requested, minor phases are not aliquoted. For samples with phases of less than 10 percent but greater than 1 percent, it will be necessary to contact SMO to prioritize the preparations and analyses to be performed, as insufficient sample may be present to perform all testing requested.

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION V

SAMPLE ANALYSIS

Method 150.20-CLP

Potentiometric and Colorimetric Determination of the pH of Industrial Waste Materials

1. Scope and Application

1.1 This method may be used to directly determine the pH of water miscible liquids or water extracted wastes. Non-water miscible phases are not analyzed.

1.2 The pH of a diluted or undiluted sample is measured by an electrode response (potentiometric method) or by an indicator test strip (colorimetric method).

1.3 The results of the direct analysis of water miscible liquids may be used for corrosivity characterization.

2. Summary of Method

2.1 Two methods are provided for the determination of the pH of wastes. The potentiometric measurement of pH by the use of a low sodium glass combination pH electrode is to be performed first. If the potentiometric measurement proves unsatisfactory due to fouling of the electrode, erratic electrode response or other sample related problems, then the colorimetric method is to be employed.

3. Interferences

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants or reductants.

3.2 Presence of organic materials in samples can impair electrode response. These materials can usually be removed from the electrode by detergent washing followed by water rinsing. Additional treatment with a organic solvent (methanol or acetone) may be necessary to remove any remaining residue.

3.3 Temperature effects on the potentiometric measurements of pH arise from two sources. The first source is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This effect is sample dependent and cannot be controlled. Therefore, both the pH and the ambient temperature at the time of analysis should be recorded.

4. Apparatus and Equipment

4.1 pH meter - capable of response to 0.05 pH units.

4.2 Low sodium glass combination pH electrode.

4.3 Magnetic stirrer and teflon-coated stirring bar.

4.4 pH paper - capable of distinguishing 0.5 pH units over pH range 0-14.

4.5 Box shaker.

4.6 Plastic disposable beakers with lids.

4.7 Disposable filter apparatus (0.45 μm).

5. Reagents

5.1 pH buffers: pH=4, pH=7, pH=10

6. Quality Control

6.1 **Preparation Blank**

6.1.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

6.1.2 Frequency

At least one PB must be prepared and analyzed with every SDG, or with each batch[1] of samples prepared, whichever is more frequent.

6.1.3 Procedure

The PB shall consist of ASTM Type II water.

The first batch of samples in an SDG is to be assigned to PB one, the second batch of samples to PB two, etc.

Compare the blank value obtained with the limit specified for ASTM Type II water ± 0.2 pH units.

6.1.4 Calculations

Not applicable.

6.1.5 Technical Acceptance Criteria

The value obtained for the blank must be within ± 0.2 pH units of the value specified for the ASTM Type II water.

[1]A group of samples prepared at the same time.

6.1.6 Corrective Action

If the value obtained is not within the required limit, all samples prepared with the blank must be reprepared and reanalyzed.

6.1.7 Documentation

Report the value obtained on FORM I-HCIN.

6.2 Duplicate Sample Analysis

6.2.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods and the matrix effects.

6.2.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[2]

6.2.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per matrix and concentration per method per SDG, if one duplicate result is not within contract criteria, flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculation of relative percent difference.

6.2.4 Calculations

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad \text{D-1}$$

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

Duplicates cannot be averaged for reporting on FORM I-HCIN.

[2]EPA may require additional duplicate sample analysis upon special requaest by the Project Officer, for which the Contractor will be paid.

6.2.5 Technical Acceptance Criteria

Compare results of the replicates to the limits ± 0.2 pH units.

6.2.6 Corrective Action

If the value for the replicates exceeds this limit, samples in that analysis group will not need to be repeated, but the results should be considered suspect and the analyst should repeat the measurements and take the appropriate steps to eliminate any problems.

6.2.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN.

6.3 Laboratory Control Sample

6.3.1 Summary

A LCS is prepared and analyzed to ensure against analyte loss in the sample preparation.

6.3.2 Frequency

A reference sample (EPA, pH concentrate), prepared according to the instructions sent with the concentrate, shall be analyzed with every set of analytical sample dilutions.

6.3.3 Procedure

The 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 LCS must be obtained from EPA. (If unavailable, other EPA Quality Assurance Check samples or other certified materials may be used.) EPA pH concentrates are available from:

EMSL/Cincinnati
Quality Assurance Branch
26 Martin Luther King Avenue
Cincinnati, OH 45268
Phone: (513/FTS) 684-7325

6.3.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-2}$$

6.3.5 Technical Acceptance Criteria

Recovery for the LCS must be within the 95 percent confidence interval (also sent with the concentrate).

6.3.6 Corrective Action

If the percent recovery for the LCS is outside the 95 percent confidence interval established by EPA, then the analyses must be terminated, the problem corrected, and the samples associated with that LCS must be reprepared and reanalyzed.

6.3.7 Documentation

Report the LCS found concentration, true concentration, and percent recovery on FORM VIII-HCIN.

7. Sample Preparation

7.1 Weigh 1.00 ± 0.1 g of sample into a disposable beaker. Dilute to 100 mL total volume with ASTM Type II water.

7.2 For water miscible phase samples, aliquot approximately 10 mL of the phase (if available) into a vial suitable for potentiometric measurement of the pH. (Do not dilute the 10 mL water miscible phase.)

7.3 Place all diluted samples on a box shaker and shake for one hour at a medium setting.

7.4 Filter all sample dilutions through disposable filter units. For dilutions with more than one phase, allow the sample dilution to settle before applying the vacuum.

7.5 Store samples at room temperature and analyze within the 24 hour time period.

NOTE: This sample can also be used for the determination of conductivity.

8. Calibration and Sample Analysis

8.1 Calibration

8.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. The analyst must be acquainted with the operation of each system and be familiar with all instrument functions. Special attention to care of the electrodes is recommended.

8.1.1.1 The stability of the calibration curve will vary with both temperature fluctuations and the sample matrices being analyzed. Therefore, a calibration check must be performed at least once every 10 sample analyses. Increasing the frequency of checking the calibration is left to the discretion of the operator.

8.1.1.2 Each instrument/electrode system must be calibrated with two buffers that bracket the expected pH of the samples. The instrument is to be calibrated as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are stable (less than 0.1 units change in one minute) and within 0.1 pH units of the buffer solution value. On the bench sheet record the pH range, slope (if available) and actual buffer readings to the nearest 0.1 pH unit.

8.1.1.3 When checking the calibration, both buffers that bracket the sample value used for calibration shall be checked and readings should agree within 0.1 units of the value sought. If the readings are not acceptable, steps shall be taken to correct the problem (e.g., recalibration, and cleaning the electrode).

8.1.1.4 When calibrating the instrument the analyst should become cognizant of the "typical" response time required for the electrode/instrument set-up in use. This is extremely important when analyzing industrial waste samples due to the possibility of sample related impairment of electrode response. The extreme pH ranges encountered in industrial waste samples can cause memory effects and other electronic problems. Also, due to the presence of organic materials in the samples, physical coating of the electrode may occur that is masked by the high ionic strength buffer measurements taken in between sample measurements.

8.2 Recalibration

8.2.1 Recalibration of the pH meter includes checking the buffers at both ends of the bracketed calibration range and adjusting the instrument if necessary. Any changes in instrument parameters (i.e., slope) should be thoroughly documented on the bench sheet along with which sample measurements correspond to which calibration.

8.2.2 If upon checking the buffer solutions the buffer value fails to read the expected pH ± 0.1 units, then all samples past the last acceptable buffer check must be reanalyzed. An exception to this rule is for a single sample analysis where, upon repeating the sample analysis and immediately checking the buffer, the buffer fails to be ± 0.1 units of the expected value. This problem may occur with samples of extreme pH or samples containing organic material.

8.3 Sample Analysis - Potentiometric Method

8.3.1 Record on the bench sheet the ambient temperature in the laboratory. It is best to perform measurements on the diluted sample phases first and then measure the pH of the undiluted water miscible phase samples.

8.3.2 Place the electrode into the sample and make certain there is sufficient volume to cover the sensing elements of the electrode.

8.3.3 Swirl the sample preparation using a stir bar while watching readout of pH meter. Continue swirling until the pH stabilizes (pH changes less than 0.1 units in one minute). Stop swirling and allow pH to stabilize again.

8.3.4 Record on the bench sheet the observed pH to a tenth of a unit (i.e., 4.0, 4.1, etc.) for pH greater than one and less than 13.0. For pH less than one or greater than 13.0, report results as "< 1.0" and "> 13.0", respectively. Rinse probe (see Section 8.6).

8.3.5 If for some reason the potentiometric measurement is questionable (i.e., erratic response, QC limits are exceeded, etc.), then repeat the measurement using the colorimetric method (Section 8.4). Document on the bench sheet the method of pH measurement.

8.4 Sample Analysis - Colorimetric Method

8.4.1 Immerse pH paper directly into a portion of the sample preparation sufficient to wet the paper thoroughly, or wet the paper by dropping the sample preparation onto the paper from a pipette.

8.4.2 Read the result of the test according to the manufacturer's instructions and record the result on the bench sheet.

8.5 Rinsing Probe

8.5.1 A slow response of the probe indicates the possibility of a fouled probe. If cleanliness is in doubt based on response time (Section 8.1.1.4), then place the probe in a calibration buffer solution and note response time. If response time is greater than usual, see Section 8.5.2.

8.5.2 Rinse the probe with a detergent solution followed by ASTM Type II water and recheck the response time. If normal, calibrate and proceed to next sample: if not see Section 8.5.3.

8.5.3 Rinse the probe with methanol or acetone followed by ASTM Type II water and check response time. If normal, calibrate and go to next sample; if not discontinue analysis until the problem is corrected. Recalibration may be required if solvents are used to clean the probe.

9. Documentation

9.1 Report the recorded pH value (to one tenth of a whole number) on FORM I-HCIN under pH.

THIS PAGE LEFT INTENTIONALLY BLANK

Method 120.1-CLP

Determination of Conductivity in Industrial Waste Material

1. Scope and Application

1.1 This method can be used to directly determine the specific conductance, in μmhos at 25°C, of water miscible liquid phases or water extracted solid phases. Non-water miscible phases are not analyzed.

1.2 The results of measuring the specific conductance can aid in estimating sample size to be used for common chemical determinations, check results of a chemical analysis, estimate total filtrable residue in a sample, and measure the corrosion rate.

2. Summary of Method

2.1 The specific conductance of a diluted or an undiluted sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.

2.2 The results of direct analyses of water miscible liquid are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.

3. Interferences

3.1 Instrument must be standardized with KCl solution before daily use.

3.2 Conductivity cells must be kept clean. If not, follow manufacturers instructions for cleaning cell to maintain a cell constant of 1.0 μmho or micro dipping type cell with 1.0 μmho constant.

3.3 Temperature variations and corrections represent the largest source of potential error. This can be controlled by allowing the sample to come to room temperature.

4. Apparatus and Equipment

4.1 Conductivity bridge, range 1 to 1000 μmho per centimeter.

4.2 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant.

4.3 Thermometer, reading in degree °C at 0.1 intervals.

4.4 Plastic disposable beakers, 100 mL.

4.5 Disposable filter apparatus (0.45 μm).

5. Reagents

5.1 Standard potassium chloride solutions, 0.01 M: Dissolve 0.7456 g of pre-dried (2 hours at 105 ± 5°C) KCl in reagent grade water and dilute to 1 L at 25°C.

6. Quality Control

6.1 Preparation Blank

6.1.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

6.1.2 Frequency

A least one PB must be prepared and analyzed with every SDG, or with each batch[3] of samples prepared, whichever is more frequent.

6.1.3 Procedure

The PB shall consist of ASTM Type II water.

The first batch of samples in an SDG is to be assigned to PB one, the second batch of samples to PB two, etc.

Compare the blank value obtained with the limit specified for ASTM Type II water ± 6 μmhos for conductivity at 25°C.

6.1.4 Calculations

Not applicable.

6.1.5 Technical Acceptance Criteria

The value obtained by the blank must be with ± 6 μmhos specified for ASTM Type II water at 25°C.

6.1.6 Corrective Action

If the value obtained is not within the required limit, all samples prepared with the blank must be reprepared and reanalyzed.

6.1.7 Documentation

Report the value obtained on FORM I-HCIN.

---

[3]A group of samples prepared at the same time.

6.2 Duplicate Sample Analysis

6.2.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods and the matrix effects.

6.2.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[4]

6.2.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per matrix and concentration per method per SDG, if one duplicate result is not within contract criteria, flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculation of relative percent difference.

6.2.4 Calculations

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad \text{D-3}$$

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

Duplicates cannot be averaged for reporting on FORM I-HCIN.

6.2.5 Technical Acceptance Criteria

Compare results of the replicates to the limits ± 6 μmhos at 25°C.

[4]EPA may require additional duplicate sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

6.2.6 Corrective Action

If the value for the replicates exceeds this limit, samples in that analysis group will not need to be repeated, but the results should be considered suspect and the analyst should repeat the measurements and take the appropriate steps to eliminate any problems.

6.2.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN.

6.3 Laboratory Control Sample

6.3.1 Summary

A LCS is prepared and analyzed to ensure against analyte loss in the sample preparation.

6.3.2 Frequency

A reference sample (EPA, conductivity), prepared according to the instructions sent with the concentrate shall be analyzed with every set of analytical sample dilutions.

6.3.3 Procedure

The 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 LCS must be obtained from EPA. (If unavailable, other EPA Quality Assurance Check samples or other certified materials may be used.) EPA conductivity concentrates are available from:

EMSL/Cincinnati
Quality Assurance Branch
26 Martin Luther King Avenue
Cincinnati, OH 45268
Phone: (513/FTS) 684-7325

6.3.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-4}$$

6.3.5 Technical Acceptance Criteria

Recovery for the LCS must be within the 95 percent confidence interval (also sent with the concentrate).

6.3.6 Corrective Action

If the percent recovery for the LCS falls outside the 95 percent confidence interval established by EPA, then the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

6.3.7 Documentation

Report the LCS found concentration, true concentration, and percent recovery on FORM VIII-HCIN.

7. Sample Preparation

7.1 Weigh 1.00 ± 0.1 g of solid phase sample into a disposable beaker. NOTE: Save water miscible phase sample aliquot for analysis, if needed. Dilute to 100 mL total volume with ASTM Type II water.

7.2 Place all diluted samples on a box shaker for one hour at a medium setting. If a sample yielded 100 mL of the water miscible phase dilutions, then there is no need to shake the sample unless a precipitate forms upon dilution. In this case, mix the non-precipitating water miscible phase dilutions thoroughly using a glass stirring rod. Treat precipitating water miscible phase sample as solids. Do not shake undiluted water miscible phases.

7.3 Filter all sample dilutions through a disposable filter units that have been pretreated by washing with high quality reagent water and pre-rinsed with sample before use. For dilutions with more than one phase, allow the sample to settle before applying the vacuum. Store samples at room temperature and analyze promptly.

NOTE: This sample preparation can also be used for the determination of pH.

8. Calibration and Sample Analysis

8.1 Calibration

8.1.1 Because of the wide variety of conductivity meters and accessories, detailed operating procedures cannot be incorporated into this method. The analyst must be acquainted with the operation of each system and be familiar with all instrument functions. Special attention to the care of the cell is vitally important!

8.1.1.1 The analyst should use the standard potassium chloride solution (5.1) and the table below to check the accuracy of the cell constant and conductivity bridge.

Conductivity 0.01M KCl degree °C	µmhos / cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

8.1.2 When checking the cell calibration, the readings should agree within ± 1.0 percent or 1 µmhos/cm, whichever is greater. If the readings are not acceptable, correct the problem and recalibrate the instrument.

8.1.3 When calibrating the instrument, the analyst should become familiar with the overall response time and the manufacturer directions for operation and maintenance of the instrument.

8.2 Sample Analysis

8.2.1 Follow the direction of the manufacturer for the operation of the instrument.

8.2.2 Allow samples to come to room temperature, approximately 23 to 27°C, if possible.

8.2.3 Determine the temperature of samples within ± 0.5°C. NOTE: If the temperature of the samples is not 25°C, make temperature correction in accordance with the instructions in Section 9 to convert readings to 25°C.

8.2.4 Place probe in solution to be measured and obtain reading as instructed by the manufacturer. Record the reading on the benchsheet.

9. Calculations

9.1 These temperature corrections are based on the standard KCl solution.

9.1.1 If the temperature is below 25°C, add 2 percent of the reading per degree.

9.1.2 If the temperature is above 25°C, subtract 2 percent of the reading per degree.

10. Documentation

10.1 Report results as Conductivity, in µmhos/cm at 25°C, on FORM I-HCIN.

Method 200.62-A-CLP

Dissolution of Industrial Waste Materials For Elemental Analysis by Potassium Hydroxide Fusion

1. Scope and Application

1.1 This method offers a vehicle to dissolve inorganic metals from a wide variety of industrial waste materials. In particular, organic matter is largely destroyed and silica matrices are dissolved.

1.2 The method has been successfully used to prepare solutions for metals analysis of oils, fats, polymers, pigments and paint, soil, sludge, sediment, fly ash, glass, and inorganic salts.

1.3 The recovery of 30 metals has been verified by this method in a number of standard reference materials.

1.4 For routine use of the method, HNO_3 is recommended although HCl may also be use for special situations (e.g.. quantitative results for silver above 100 mg/Kg), if the laboratory can demonstrate that the use of HCl results in meeting the QC requirements.

1.5 All samples shall be carried through the sample preparation procedure and then run undiluted. When an analyte concentration exceeds the calibrated or linear range, appropriate dilution and reanalysis of the prepared sample is required. The dilution factor shall not bring the concentration below the CRQL. All dilutions shall be taken from the original sample, diluting previously diluted samples are not acceptable.

2. Summary of Method

2.1 A 0.25 g aliquot of sample is fused with 2 g of potassium hydroxide in a pyrolytically-coated graphite crucible. Commercial potassium hydroxide usually contains about 15 percent by weight of water. Water appears to help destroy organic matter by hydrolysis reactions. In addition, the water appears to lower the melting point of the mixture to about 125°C although the KOH may be dissolving in the residual water at this temperature to mimic melting. The water-potassium hydroxide melt is formed during heating in a block digester. The temperature of the melt is increased slowly so that vigorous oxidation reactions between organic matter and the fusion matrix can be controlled. The temperature is increased to 360°C, and the melt solidifies as the water evaporates. The crucibles are then heated in an electric furnace in which anhydrous KOH (and K_2CO_3 from absorbed CO_2) melts at around 400°C, depending upon the amount of K_2CO_3 and other dissolved matter from the sample. The higher temperatures of the melt subject the sample to an oxidizing environment, perhaps due to the partial transformation of KOH to K_2O. The final temperature of the melt should be 525°C.

2.2 The cooled fusion mass is rinsed from the crucible into a beaker. Nitric acid is warmed in the crucible and then rinsed into the beaker. Hydrogen peroxide reduces Cr (VI) to Cr (III), in order to avoid precipitation of insoluble metal chromates. When titanium is present in high concentrations, an orange peroxide $[Ti(O_2)(OH)_{aq}]^+$ complex is formed with the peroxide. The peroxide addition may also aid in the dissolution or stabilization of B, Co, Mn, Mo, Si, W, and other elements. The solution is mixed overnight to aid dissolution and to outgas the peroxide. The final dilution volume is 100 mL.

2.3 The spike sample is prepared by adding 0.0125 g of the solid spiking mixture to a 0.25 g aliquot of sample which is then carried through the sample preparation procedure.

2.4 A preparation blank is prepared for each sample phase as follows:

2.4.1 Water miscible phase: The preparation blank for the water miscible phase consists of 0.25 g of ASTM Type II water which is carried through the sample preparation procedure.

2.4.2 Non-water miscible phase: The preparation blank for the non-water miscible phase is a reagent blank.

2.4.3 Solid phase: The preparation blank for the solid phase is a reagent blank.

3. Apparatus and Equipment

3.1 Electric furnace - temperature controlled to at least 550°C.

3.2 Block digester - temperature controlled to at least 360°C; hole size 25 mm diameter.

3.3 Exhaust hood or suitable venting system.

3.4 Rotary shakers (two), variable speed.

3.5 Pyrolytically-coated graphite crucibles (Ultra Carbon, Bay City, Michigan, #UF-45 with PT-101 coating, or equivalent).

3.6 Handling tongs - platinum tipped.

3.7 Hot plate - preferably ceramic top.

3.8 Disposable biological membrane filters (0.45 μm) or membrane filter apparatus and filters (0.45 μm).

3.9 Disposable plastic 8 oz. bottles with lids.

4. Reagents

4.1 Potassium hydroxide, reagent grade.

4.2 Nitric acid, concentrated, reagent grade.

4.3 Hydrochloric acid, concentrated, reagent grade.

4.4 Hydrogen peroxide, 30 percent.

5. Sample Preparation and Handling

5.1 Samples are processed through the phase separation procedure (Method 50.60-CLP). Waste samples are not generally dried; results will be reported on a wet weight basis. Phases of a sample will be prepared and analyzed individually.

6. Procedure

6.1 Preheat block digester to 160°C. To facilitate placement or removal of the crucibles in or from a standard total nitrogen block digester, drop old empty crucibles in the holes (crucibles open side up) to make up extra space. The digester sits on the rotary shaker.

6.2 Place a new crucible on clean paper on an analytical balance; tare the crucible.

6.3 Weigh 0.250 ± 0.015 g of an analytical sample into a crucible. If the sample should get on the crucible lip or outside walls, a new sample aliquot should be weighed into a new crucible.

6.4 Add 2.0 ± 0.1 g of KOH to the crucible.

6.5 When all the crucibles contain sample and KOH, place the crucibles in the block digester.

6.6 Heat the sample preparations at 160°C in the block digester for 30 minutes, with constant swirling provided by the rotary shaker moving at 100 RPM. Samples containing high concentrations of organic matter may evolve CO_2 and cause bubbling over of the fusion. To prevent this from occurring, manually swirl each crucible at least once every 15 minutes using the platinum tongs. (Turn off shaker to remove crucibles.)

6.7 After heating the preparations at 160°C for 30 minutes, set the block controller to 360°C and continue heating the preparations until they are dry. This step usually takes at least 90 minutes. NOTE: The sample must mixed every 15 minutes by gently swirling the crucible to avoid possible creeping or spattering of the sample.

6.8 During the latter part of the 360°C heating step, preheat the electric furnace to 425°C.

6.9 After the fusion melts have dried and solidified, transfer the crucibles to the furnace (which also sits upon a rotary shaker moving at 100 RPM). Heat the samples for 15 minutes at 425°C, followed by heating for 20 minutes at 525°C. Make sure that the crucibles do not touch each other. The required temperature setting is critical and may vary from furnace to furnace. The temperature should be high enough to allow Chromium recovery from the NIST LCS to be within the contract acceptance limits, but low enough to minimize sample creeping. The contractor shall maintain a record demonstrating that the furnace has been properly calibrated prior to use.

6.10 Remove the crucibles from the furnace.

6.11 When the crucibles are removed, it may be evident that some of the fusion melts have crept up and over the lip of the crucible. If the creeping has progressed to within one-half inch of the outside bottom of the crucible, the preparation must be discarded and another fusion shall be performed on the analytical sample. If the creeping persists for a certain sample, the fusion time at 525°C may be shortened, or the high furnace temperature lowered to 475-500°C. Another option is to top the crucible with a lid made from the bottom of another crucible. If any options are used, a set of quality control samples must be prepared under the same conditions.

6.12 Using ASTM Type II water, rinse all deposits from the outside and lip of the crucible into an 8 oz. plastic beaker. Fill the crucible with reagent water. This often loosens the fusion product so that it

falls out as one piece. After the ASTM Type II water has been in the crucible for a few minutes, rinse all the fusion product out of the crucible and into the cup with ASTM Type II water. Do not use more than 70 mL ASTM Type II water. If it appears that the fusion product is not going to be removed with 70 mL of ASTM Type II water, then crush the fusion product in the crucible with a teflon or glass rod and rinse the pieces of the fusion product in the crucible and on the rod into the beaker. Record on the bench sheet the color of the solution in the beaker.

6.13 Fill the crucibles with approximately 7 mL of concentrated nitric acid and place the empty crucibles on a hot plate set at 95°C. Heat until acid fumes are apparent.

6.14 Carefully pour the nitric acid from the crucibles into the disposable beakers. Carbon dioxide may be released, so be cautious. Rinse the crucible with a minimum of reagent water and combine the rinse with the solution in the disposable beaker.

6.15 Add an additional 3 mL of concentrated nitric acid to each beaker. Record on the bench sheet the color of the solution in each beaker.

NOTE: The high concentration of acid in the solution at this point may cause some metals to become insoluble. Therefore, sufficient ASTM Type II water must be added at this time to bring the total volume to a minimum of 50 mL.

6.16 If the fusion product does not readily dissolve, cap the beaker and shake it on the shaker at 100 RPM for a maximum of 30 minutes, or until it is dissolved.

6.17 Add 1 mL of 30 percent hydrogen peroxide to each solution. Record the color change of the solution in each beaker when peroxide is added on the bench sheet. Cap and shake the solutions on the shaker at 100 RPM overnight. During the first few hours, vent the beakers periodically.

6.18 Quantitatively transfer each solution to a disposable filter apparatus and apply a vacuum. After the solution has been filtered into a graduated vessel, rinse the filter with ASTM Type II water and add the rinse to the filtered solution. Record on the bench sheet the presence of any residue on the filter and describe it.

6.19 Using ASTM Type II water, dilute the filtered solution to 100 mL using the marks on the graduated cylinder. If prior to the volume adjustment the volume is greater than 100 mL, dilute the solution to 115 mL. Record the final volume of each solution on the bench sheet.

6.20 If the solution requires shipment for analysis, transfer the solution to an acid-washed shipping container and label appropriately. Solutions are now ready for analysis.

7. Documentation

7.1 Report the EPA Sample number, preparation date, sample weight (in grams), volume (in mLs), color and clarity on FORM XIV-HCIN.

Method 200.62-B-CLP

Pneumatic Nebulization Inductively Coupled Argon Plasma Optical Emission Spectroscopic (ICP) Analysis

1. Scope and Application

1.1 This method is applicable to the ICP determination of 18 metals dissolved by the potassium hydroxide (KOH) fusion (Method 200.62-A-CLP) at all concentrations.

1.2 The 18 metals to be determined include: aluminum, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, silver, sodium, thallium, vanadium, and zinc.

2. Summary of Method

2.1 Inductively Coupled Argon Plasma Optical Emission Spectroscopic (ICP) Analysis is used for the determination of 18 metals. The potassium hydroxide fusion dissolutions of the samples are pumped into a pneumatic nebulizer. The aerosol formed is transported into an inductively coupled plasma and the metals are excited into higher electronic states. Atomic and ionic line emission spectra characteristic of the particular metals are produced when the electrons decay back to the lower energy levels. The spectra are dispersed by a spectrometer and the intensity of specific line radiation(s) are monitored simultaneously or sequentially by a photomultiplier tube(s). The photocurrent produced by the photomultiplier tube will increase in direct proportion to the concentration of the element in the sample within the linear range of a specific emission line. The photocurrent is processed by a computer system and related to concentration through a calibration procedure.

2.2 Calibration is performed by standardizing the instrument with a series of mixed element standards and a blank that are matrix matched to the potassium hydroxide fusion dissolution. Every solution analyzed, such as a dilution, calibration stability standard, or reference sample must be matrix matched to the fusion dissolution.

2.3 Appropriate steps must be taken to ensure that potential interferences are corrected. This is especially important for spectral interferences. Recommendations for correcting for interferences are briefly summarized below under headings that categorize the type of interference that is being considered. Section 7 contains requirements for the operation of the ICP.

2.3.1 Physical Interferences

- The use of peristaltic pump to introduce the fusion solution into the nebulizer.
- Frequent (20 percent or better) analysis of the calibration stability standard.
- Adequate rinsing (one minute or more) between sample analyses using 10 percent HNO_3 or 10 percent HCl, and optional use of humidified argon or a nebulizer tip washer as necessary.

2.3.2 Chemical Interferences

- Matrix matching between fused samples and all standards and sample dilutions is used in sample analysis. The high potassium concentration of the fusion matrix helps to eliminate ionization interferences.

2.3.3 Spectral Interferences

- Use of calculated interelement corrections in the form of factors or first or second order equations that describe the interference function (on-peak correction).
- Optional use of measurement of background shift on either side or both sides of the analyte line (off-peak correction).
- Optionally, wavelength scans (for each of the analyte element wavelengths) for each of the samples simultaneously plotted with a calibration blank scan and a calibration standard scan may be performed.

2.4 Every solution, including calibration standards, calibration and method blanks, reference samples, and fused samples must be analyzed using two full exposures (peak scan), each of which is sufficient to meet the method detection limit for each analyte emission line. All exposure times must be the same for all analyses and all quarterly analyses (i.e., method detection limit and interelement correction factor).

2.5 Both the off-peak (background) and on-peak (interelement correction coefficients or equations) interference corrections made for all metals must be calculated and reported with the analysis results.

2.6 If the sum of the values of the interference correction(s) made on any metal is greater than the resulting metal concentration, the metal value is to be flagged with an "I" on FORM I-HCIN.

2.7 If the analyte requiring dilution interferes on with another metal, the interference correction(s) must reflect the actual concentration of the interferant in the undiluted samples.

2.8 The specific spectral lines that are employed must be reported.

2.9 All reported analyte data must have been obtained within the linear range of the respective analyte emission line. If any analyte concentration results in the linear range of the spectral line being exceeded, the sample must be diluted such that the resulting solution concentration falls within the linear range, but not below the CRQL.

2.10 If a value for silver found in the HNO_3 preparation is greater than 100 mg/Kg, the sample must be reprepared and reanalyzed using HCl in place of the HNO_3 for sample dissolution.

3. Interferences

3.1 Inductively coupled argon plasma emission spectroscopy is prone to interelement effects, which in practice are experienced in two main forms. Interferences that cause a translation of the analytical curve are caused by spectral line overlap or increase in background due to an electron/metal ion recombination continuum and/or scattered light within the spectrometer. For a given matrix and spectral line, a constant additive interference is produced that is independent of the analyte concentration. Rotational interference of the analytical curve, experienced essentially as a change in sensitivity, is due to the combined effects of variations in nebulizer performance produced by the physical properties of the sample solution and changes in the excitation conditions in the plasma caused by the matrix metals. Both forms of interference can operate simultaneously for a particular sample matrix.

3.2 Spectral interference from poorly resolved metal spectral lines, such as scattered light, or broad continuum spectral background, will lead to systematic error in the analytical results unless proper corrections are made. Molecular band emission will lead to a deterioration of the detection limit and will increase the difficulty of off-peak background correction. Methods of correcting translational interference (other than exact matrix matching of the standards to the sample) include the on-peak correction technique. This method can be applied to both spectral line overlap and background enhancement, but it requires specific knowledge of the metals causing the interference. On-peak correction can only be performed on a quantitative basis if the interfering metals are included in the multi-metal analysis, although uncertainties may still exist in whether the correction coefficients employed match those required for the particular sample matrix.

3.3 Rotational calibration curve interference manifests itself for a given matrix and spectral line as a change in the slope of the analyte calibration. Included in this type of interferences are: sample nebulization and transport effects, often called "physical interference" including "lateral diffusion interferences;" and "chemical interferences" such as "solute vaporization interference" and "ionization interferences." Such interferences can be reduced by matrix matching of the standards and samples and by the method of standard additions, although standard additions can become quite lengthy and impracticable for multi-metal analyses. Matrix matching can correct for any of these interferences but the correction is dependent on the accuracy of the matching. Variations in the matrix from sample to sample will cause corresponding inaccuracies in the analyte results. However, since an abundance of potassium is present in both samples and standards, rotational interferences are largely eliminated by matrix matching.

4. Apparatus and Equipment

4.1 Computer-controlled inductively coupled argon plasma optical emission spectrophotometer system with:

4.1.1 Polychromator with associated dispersion and detector system such that the metals can be determined simultaneously, or a sequential scanning instrument that allows achievement of the quality control requirements for this method.

4.1.2 Radiofrequency generator and coupling system.

4.1.3 Pneumatic nebulizer.

4.1.4 Software capable of performing both off-peak (background correction) and on-peak (coefficients of first or second order regression equations describing expected interference) spectral interference corrections. In addition, the software must be capable of creating a hardcopy output of both types of corrections in either concentration units or analyte raw intensity data along with net calculated concentrations.

4.2 Argon gas supply, welding grade or better.

4.3 Assorted laboratory volumetric glassware, pipets and micropipets.

4.4 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.

5. Reagents and Standards

5.1 Nitric acid and hydrochloric acid used in the preparation of standards and for sample processing must be of high purity.

5.2 Potassium hydroxide, ACS reagent grade.

5.3 Water equivalent to ASTM Type II is used throughout.

5.4 Stock standard solutions - Standards must be made from ultrapure materials. The stock standard solutions may be the same as the spiking standard solutions, if desired.

5.5 Spiking standard solutions - Standards must be made from ultrapure materials. Both multi-metal and single metal solutions will be needed. Because of the limited sample volume (100 mL), multi-metal solutions will be needed to maintain the sample matrix at 95 percent original strength after the addition of the spike volume.

5.5.1 No more than five multi-metal stock standards will be required containing metals in the following concentrations:

Metals	Conc. (mg/L)
Na	10000
Al, Ca, Fe, Mg	1000
Ba, Co, Mn. Ni, Pb, Ag. Tl, V	500
Be, Cd, Cu, Cr, Zn	100

5.5.2 Using the appropriate metal salts and solution matrices, the following standards have been found to be stable for one year.

Metal Mixes	Matrix
Al, Ba, Be, Fe, Ni, Ag, Na, Tl	20% conc. HCl
Ca, Cd, Co, Cu, Pb, Mg, Mn, Zn	10% conc. HNO_3
Cr	Water
V	2% conc. HNO_3

5.5.3 A single metal standard at 10,000 mg/L will be needed for Na and at 1,000 mg/L for the remaining metals.

5.6 Calibration standards - Prepare calibration standards by dilution of stock or spiking standard solutions. All calibration standards must contain 2 g of KOH and 10 mL of concentrated HNO_3 per 100

mL. Concentrated hydrochloric acid can be used instead of HNO_3 if required for stabilization of a metal(s). It is convenient to prepare a solution containing 4 g of KOH and 20 mL of HNO_3 per 100 mL, using 50 mL of this solution per 100 mL in the preparation of the standards.

5.7 Calibration blank - Prepare calibration blanks such that the resulting solution contains 2 g of KOH and 10 mL of concentrated HNO_3 per 100 mL.

5.8 Initial calibration verification - The initial calibration verification solution must be from a different source than that used for the calibration standards and must be approximately in the middle of the respective calibration curve.

5.9 ICP interference check sample - Prepare by dilution of the stock standards if it is not available from the EPA. If the solution is prepared by the analyst, it must be made using the concentrations in Table 2 of Exhibit C. It must be run at least five times and the mean standard deviation must be reported in the raw data.

6. Quality Control

6.1 Instrument Calibration

6.1.1 Summary

Prior to the analysis of samples and required QC, each ICP system must be initially calibrated to determine instrument sensitivity.

6.1.2 Frequency

Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

6.1.3 Procedure

Calibration standards must be prepared using the same type of matrix and at the same concentration as the preparation blank following sample preparation.

Calibrate according to instrument manufacturers recommended procedures using at least two standards, one being a blank.

6.1.4 Calculations

Not applicable.

6.1.5 Technical Acceptance Criteria

Not applicable.

6.1.6 Corrective Action

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 a CCV and a CCB.

6.1.7 Documentation

The instrument standardization date and time must be included in the raw data.

6.2 Initial Calibration Verification

6.2.1 Summary

Immediately after the ICP system has 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) (ICV) at each wavelength used for analysis.

6.2.2 Frequency

Each time the instrument is calibrated, the ICV must be run immediately following the calibration, before any samples are analyzed.

6.2.3 Procedure

If the ICV 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 linear 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.

6.2.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-5}$$

6.2.5 Technical Acceptance Criteria

Recovery for the ICV must be within ± 10 percent of the true value (i.e., 90-110%). (See Table 2, Exhibit C)

6.2.6 Corrective Action

When recoveries of the ICV exceed the technical acceptance criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

6.2.7 Documentation

Report the ICV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.3 Continuing Calibration Verification

6.3.1 Summary

To ensure calibration accuracy during an analysis run, a continuing calibration verification solution (CCV) is analyzed and reported for every wavelength used for the analysis of each analyte.

6.3.2 Frequency

The CCV is run at a frequency of 10 percent or every two hours during an analysis run, whichever is more frequent.

The CCV is also run after the last analytical sample in the analysis run.

6.3.3 Procedure

The same CCV must be used throughout the analysis runs for a Case of samples received.

The analyte concentrations in the continuing calibration standard must be one of the following solutions and should be at or near ± 10 percent the mid-range levels of the calibration curve:

- EPA solutions; or
- A Contractor prepared standard solution.

Each CCV analyzed must reflect the conditions of analysis for all of the 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.

6.3.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-6}$$

6.3.5 Technical Acceptance Criteria

Recovery for the CCV must be within ± 10 percent of the true value (i.e., 90-110%).

6.3.6 Corrective Action

When recoveries of the CCV exceed the technical acceptance criteria, the analysis must be stopped, the problem corrected, the instrument recalibrated, the calibration reverified, and the preceding 10 analytical samples reanalyzed (or all analytical samples since the last "acceptable" CCV analyzed).

6.3.7 Documentation

Report the CCV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.4 CRQL Standard

6.4.1 Summary

To verify linearity near the CRQL, the Contractor must analyze an ICP standard at two times the CRQL or two times the MDL, whichever is greater. This standard must be run for every wavelength used for analysis.

6.4.2 Frequency

The CRQL standard must be run at the beginning and end of each sample analysis run, or a minimum of twice per eight hours, whichever is more frequent.

6.4.3 Procedure

The CRQL standard is not to be run before the ICV solution.

6.4.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-7}$$

6.4.5 Technical Acceptance Criteria

Recovery of the CRQL standard must be within ± 25 percent of the true value (i.e., 75-125%) for each wavelength used for analysis. (See Table 3, Exhibit C)

6.4.6 Corrective Action

If the CRQL standard does not fall within the control limit, the analysis must be terminated and the problem corrected and the analytical samples since the last acceptable CRI must be reanalyzed.

6.4.7 Documentation

Report the CRQL standards found concentration, true concentration, and percent recovery on FORM III-HCIN.

6.5 Linear Range Analysis

6.5.1 Summary

The concentration range over which the ICP calibration curve remains linear must be determined and any values above this linear range, must be diluted and reanalyzed.

6.5.2 Frequency

For all ICP analyses, a linear range verification check standard (LRS) must be analyzed within 30 days of the start of the contract and at least quarterly (every three calendar months) until the end of the contract. This standard must be run for all wavelengths used for each analyte reported by ICP.

6.5.3 Procedure

The standard must be analyzed 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).

6.5.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-8}$$

6.5.5 Technical Acceptance Criteria

Recovery for the LRS must be within ± 5 percent of the true value (i.e., 95-105%).

6.5.6 Corrective Action

If the recovery of the LRS does not meet the technical acceptance criteria, then the analysis must be terminated and successive dilutions of the standard must be reanalyzed until the control limits are met. The concentration of this standard that meets the control limits is the upper limit of the instrument linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

6.5.7 Documentation

Report the LRS found concentration (in mg/L), true concentration (in mg/L) and percent recovery for each metal on FORM III-HCIN.

6.6 Initial Calibration Blank

6.6.1 Summary

To verify that the ICP system is not contaminated, an initial calibration blank (ICB) must be analyzed after calibration.

6.6.2 Frequency

The ICB must be analyzed each time the system is calibrated and immediately after the ICV.

6.6.3 Procedure

If the absolute value of the ICB is greater than the MDL, the result must be reported.

6.6.4 Calculations

Not applicable.

6.6.5 Technical Acceptance Criteria

The absolute value of the ICB must be less than the CRQL.

6.6.6 Corrective Action

When the ICB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the ICB.

6.6.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

6.7 Continuing Calibration Blanks

6.7.1 Summary

To ensure that the system is not contaminated during the analysis run, continuing calibration blanks (CCB) are analyzed.

6.7.2 Frequency

Analyze the CCB at a frequency of 10 percent or every two hours, whichever is more frequent.

Analyze the CCB after every CCV.

6.7.3 Procedure

A CCB must be run after the last CCV in the analysis run.

If the absolute value of the CCB is greater than the MDL, the result must be reported.

6.7.4 Calculations

Not applicable.

6.7.5 Technical Acceptance Criteria

The absolute value of the CCB must be less than the CRQL.

6.7.6 Corrective Action

When the CCB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCB analyzed).

6.7.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

6.8 Preparation Blanks

6.8.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

6.8.2 Frequency

At least one PB, must be prepared and analyzed with every SDG, or with each batch[5] of samples digested, whichever is more frequent.

6.8.3 Procedure

The PB shall consist of ASTM Type II water processed through each sample preparation and analysis procedure step (See Exhibit D, Section III).

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.

6.8.4 Calculations

Not applicable.

6.8.5 Technical Acceptance Criteria

The absolute value of the PB must be less than the CRQL.

6.8.6 Corrective Action

If the absolute value of the concentration of the blank is less than or equal to the CRQL, no correction of sample results is performed.

[5]A group of samples prepared at the same time.

If any analyte concentration in the blank is above the CRQL, all associated samples containing less than ten times the blank concentration must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

If an analyte concentration in the blank is below the negative CRQL, then all samples reported below ten times CRQL associated with the blank must be redigested and reanalyzed.

6.8.7 Documentation

The values for the preparation blank must be recorded in mg/Kg on FORM IV-HCIN.

6.9 ICP Interference Check Sample

6.9.1 Summary

To verify interelement and background correction factors, an ICP Interference Check Sample (ICS) is analyzed.

6.9.2 Frequency

Analyze the ICS at the beginning and end of each analysis run or a minimum of twice per eight hour working shift, whichever is more frequent, but not before the ICV.

6.9.3 Procedure

The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferants, and Solution AB consists of the analytes mixed with the interferants. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

The ICP ICS must be obtained from EPA (EMSL-LV) if available and analyzed according to the instructions supplied with the ICS.

If the ICP ICS is not available from EPA, independent ICP check samples must be prepared with interferant and analyte concentrations at the levels specified in Table 2 - ICP Interference Check Sample (see Exhibit C). The mean value and standard deviation must be established by initially analyzing the check samples at least five times repetitively for each parameter

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).

6.9.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-9}$$

$$Mean = \bar{X} = \sum_{i=1}^{n} X_i / n \qquad \text{D-10}$$

$$Standard\ Deviation = \sigma = \sqrt{\sum_{i=1}^{n} (X_i - \bar{x})^2 / (n - 1)} \qquad \text{D-11}$$

6.9.5 Technical Acceptance Criteria

Recovery for the ICS must be within ± 20 percent of the true value (i.e., 80-120%).

6.9.6 Corrective Action

If the ICS recoveries do not meet the technical acceptance criteria, terminate the analysis, correct the problem, recalibrate the instrument, verify the calibration, and reanalyze all of the analytical samples analyzed since the last acceptable ICS.

6.9.7 Documentation

Report the ICS found concentration, true concentration, percent recovery, mean and standard deviation on FORM V-HCIN.

The mean and standard deviation must be reported in the raw data.

6.10 Spike Sample Analysis

6.10.1 Summary

To provide information about the effect of the sample matrix on the digestion, a known amount of analyte is added (spiked) into a sample.

6.10.2 Frequency

At least one spike sample analysis must be performed on each group of samples of a similar phase for each SDG.[6]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., ICP, HYICP, GFAA, etc.), then the spike samples must be run by each method used.

[6] EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

6.10.3 Procedure

The spike is added before the sample preparation (i.e., prior to fusion, digestion or distillation).

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.

In the instance where there is more than one spike sample per phase 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.

6.10.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-12}$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

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 6.12, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery.

When the sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating percent recovery.

6.10.5 Technical Acceptance Criteria

Recovery for the spike should be within ± 25 percent of the spiked amount (i.e., 75-125%).

6.10.6 Corrective Action

If the spike recovery is not within the limits of 75-125 percent, 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-HCIN and VII-HCIN.

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 percent recovery criteria.

6.10.7 Documentation

Report the spiked sample results, sample results, spike added and percent recovery for the spike sample analysis on FORM VI-HCIN.

The units for reporting spike sample results will be in mg/Kg.

6.11 Analytical Spike Sample Analysis

6.11.1 Summary

To provide information about the effect of the sample matrix on the measurement system an analytical spike analysis is performed.

6.11.2 Frequency

At least one spike sample analysis must be performed on each group of samples of a similar phases for each SDG.[7]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., ICP, HYICP, GFAA, etc.), then spike samples must be run by each method used.

6.11.3 Procedure

The analytical spike sample analysis must be performed on a sample containing measurable amounts of the analytes or at least a representative sample of the phases associated with it.

The spike is added after the sample preparation and prior to analysis.

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 spiked with a concentration equal to 30 percent of the analytes linear range.

The sample and spiked sample must be at the same dilution.

In the instance where there is more than one spike sample per phase 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.

[7] EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

6.11.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-13}$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

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 6.12, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery.

When sample concentration is less than the method detection limit, use SR = 0 only for purposes of calculating percent recovery.

6.11.5 Technical Acceptance Criteria

Recovery for the analytical spike should be within ± 15 percent of the spiked amount (i.e., 85-115%).

6.11.6 Corrective Action

If the spike recovery is not at or within the limits of 85-115 percent, a second analytical spike must be performed. If the second analytical spike is out of control, then the preparation blank must be spiked with the same spiking solution. If spiking the blank yields a recovery that is out of control, the spiking solution must be reprepared and the previous spiking procedure repeated. If not, then flag all samples received associated with that spike sample and determined by the same analytical method with the letter "E" on FORMs I-HCIN and VII-HCIN.

6.11.7 Documentation

Report the spiked sample results, sample results, spike added and percent recovery (positive, negative, or zero) for the analytical spike sample analysis on FORM VII-HCIN.

The units for reporting analytical spike sample results will be in mg/L.

6.12 Duplicate Sample Analysis

6.12.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods as well as matrix effects.

6.12.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[8]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., HYICP, GFAA, etc.,), then duplicate samples must be run by each method used.

6.12.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per matrix and concentration per method per SDG, if one duplicate result is not within contract criteria, flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculations of relative percent difference.

6.12.4 Calculations

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad \text{D-14}$$

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

Duplicates cannot be averaged for reporting on FORM I-HCIN.

6.12.5 Technical Acceptance Criteria

A control limit of ± 20 percent for RPD shall be used for original and duplicate sample values greater than or equal to five times CRQL (Exhibit C). A control limit of ± the CRQL must be used for sample values less than five times CRQL.

If one result is above the five times CRQL level and the other is below, use the ± CRQL criteria.

If both sample values are less than the MDL, the RPD is not calculated.

Specific control limits for each metal will be added to FORM IX-HCIN at a later date based on precision results.

[8] EPA may require additional duplicate sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

6.12.6 Corrective Action

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk "*".

6.12.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN in mg/Kg.

The absolute value of the control limit (CRQL) must be entered in the "CONTROL LIMIT" column on FORM VIII-HCIN.

6.13 Laboratory Control Samples

6.13.1 Summary

A LCS is digested and analyzed to ensure against analyte loss in the sample preparation.

6.13.2 Frequency

One LCS must be prepared and analyzed for every group of samples in a SDG, or for each batch of samples, whichever is more frequent.

6.13.3 Procedure

The 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 LCS must be obtained from EPA. (If unavailable, other EPA Quality Assurance Check samples or other certified materials may be used.)

6.13.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-15}$$

6.13.5 Technical Acceptance Criteria

Recovery for the LCS must be within ± 20 percent of the true value (i.e., 80-120%).

6.13.6 Corrective Action

If the percent recovery for the LCS falls outside the limit established by EPA, then the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

6.13.7 Documentation

Report the LCS found concentration (in mg/Kg), true concentration (in mg/Kg). and percent recovery on FORM IX-HCIN.

6.14 Method Detection Limits

6.14.1 Summary

The method detection limit (MDL) must be determined before any samples are analyzed for every instrument that will be used.

6.14.2 Frequency

MDLs must be determined within 30 days of the start of the contract and at least quarterly (every three calendar months) until the end of the contract.

6.14.3 Procedure

The Method Detection Limits (in mg/L) shall be determined by multiplying by three, the average of the standard deviations (σ_{n-1}) obtained on three nonconsecutive days from the consecutive analysis of seven different preparation blank dissolutions. 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). MDLs must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined MDL for an instrument must always be used as the MDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the MDL, the MDL for that instrument must be redetermined and the results submitted for use as the established MDL for that instrument for the remainder of the quarter.

MDLs must be determined in mg/L.

6.14.4 Calculations

$$MDL = (\sigma_{n-1}) \times 3 \qquad \text{D-16}$$

6.14.5 Technical Acceptance Criteria

The MDLs must be able to meet the CRQL's established in Exhibit C.

6.14.6 Corrective Action

If an instrument's MDL cannot meet the CRQL for an analyte, that instrument cannot be used to quantitate an analysis unless the analyte concentration is greater than or equal to two times the reported MDL.

6.14.7 Documentation

MDLs must be reported for each instrument used on FORM XI-HCIN submitted with each data package. If multiple instruments are used for the analysis of an analyte within a SDG, the highest MDL for the analyte must be used for reporting concentration values for that SDG.

6.15 Interelement Correction Factors

6.15.1 Summary

To ensure against spectral interferences, interelement correction factors are determined for all wavelengths used for each analyte reported by ICP.

6.15.2 Frequency

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined within three months prior to the start of contract analyses and at least annually thereafter.

6.15.3 Procedure

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.

Follow the instrument manufacturer's recommendations for applying interelement correction factors.

6.15.4 Calculations

Not applicable.

6.15.5 Technical Acceptance Criteria

Not applicable.

6.15.6 Corrective Action

Not applicable.

6.15.7 Documentation

Results from interelement correction factors determination must be reported on FORM XII-HCIN for all ICP parameters.

7. Instrument Operation

7.1 No detailed operating instructions as to the optimization of the plasma power, argon flows, torch and coil configuration, etc. will be given. The analyst should follow the instructions provided by the manufacturer of the particular instrument.

7.2 The sample introduction system is to be of a pneumatic type. The use of a peristaltic pump instead of direct aspiration is required because of the high salt content of the fusion dissolutions. A tip washer is a very useful aid and can be easily inserted into the sample flow system by placing a "tee connector" on the carrier argon flow line just before entering the nebulizer. One arm of the "tee connector" runs to the nebulizer, another to the carrier argon flow line and the third is connected to a line from the peristaltic pump. When a drop in the carrier flow is observed, a small pulse of water is pumped into the carrier argon flow and blown through the nebulizer orifice, dissolving the salt buildup and restoring the original carrier argon flow.

7.3 Changes in the carrier argon flow may change the emission characteristics of the analyte. The use of a digital mass flow controller on the carrier argon flow is recommended to control the flow, rather than the use of a rotometer.

7.4 For direct reading instruments, every solution, including calibration standards, calibration and method blanks, reference samples, and fused samples must be analyzed using two full exposures (peak scan), each of which is sufficient to meet the method detection limit (at each analyte emission line). All exposure times must be the same for all analyses and all quarterly analyses (i.e., method detection limit and interelement correction factor.) Each background spectral region must have an exposure time equivalent to a full exposure time for direct reading instruments.

7.5 Selection of the appropriate background spectral region for each analyte must account for the major interferants within that region and for the possibility of analyte line broadening at high concentrations.

> 7.5.1 One of the best ways to select the appropriate background spectral region is to perform a wavelength scan around the analyte wavelengths in the presence of metals frequently encountered at high levels in the samples. Alternately, if the instrument does not have automatic scanning capability, selection of the background spectral region will have to be determined on the basis of manual scans and experience.
>
> 7.5.2 It is possible, if the background correction wavelength is too close to the analyte line, to observe either a net intensity of zero or other erroneous net intensity readings. To aid in circumventing this error, it is required, at a minimum, that uncorrected analyte concentrations can be derived from the submitted raw data package. In addition, the equivalent concentration correction determined at the background correction wavelength must be reported. Finally, all uncorrected intensity data for all analyte lines and background correction wavelengths must be reported. The analyst must review this data prior to submission to assure that reported values do not reflect this type of error.

7.6 Rinsing between sample/standard solutions is extremely important to help alleviate salt build-up at various points in the sample introduction system and to eliminate carry-over between samples. A high level of potassium may cause salting out at various points in the nebulizer or torch. This problem is

intensified when the solutions are nebulized for extended periods of time. Rinse with 10 percent HNO_3 and 10 percent HCl. Do not aspirate the calibration blank between sample aspirations as a "wash" mechanism. A minimum rinse time of at least one minute between samples must be used.

7.7 The determination of the linear range of each analyte line, interference effects, and any type of detection limit or precision measurement must be established under the same conditions used for the analysis of the samples, including the background correction scheme.

8. Sample Analysis

8.1 Calibration

8.1.1 Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning analysis. This requires at least 30 minutes of operation with the plasma lit prior to calibration.

8.1.2 Initiate appropriate operating configuration of the instrument computer.

8.1.3 Perform the appropriate steps recommended by the manufacturer to align the exit slits with the entrance slit. These steps are commonly called the profile or wavelength calibration procedure.

8.1.4 Calibrate the instrument using the appropriate matrix matched calibration standard solution(s). The number of standards utilized is left to the discretion of the operator but must include a calibration blank and at least one calibration standard. The operator should be aware of the requirements in Exhibits D and E that provide for the assurance that all sample values are within the linear range of the initial calibration.

8.2 Analysis Sequence

8.2.1 Before beginning the sample analysis run, analyze the initial calibration blank (ICB), initial calibration verifications (ICV), interference check sample, and CRQL standard (CRI). The ICV concentration values must not deviate from the actual values by more than 10 percent. The CRI concentration must not deviate from the actual value by more than 25 percent. The calibration blank values may not exceed the CRQL. The interference check sample found values may not deviate by more than 20 percent of the true values. If these conditions are not met for any metal, the analysis shall be discontinued (see Exhibits D (Quality Control- Initial and Continuing Calibration Blanks) and E for additional information).

8.2.2 Upon successful analysis of the ICV, ICB, CRI, and ICS, analyze all method blank dissolution(s) prepared with the fused samples. If any of the blank(s) values are not less than or equal to the CRQL, see Exhibits D and E for the appropriate action.

8.2.3 If the method blank(s) values are acceptable, analyze the Laboratory Control Sample (LCS). If any of the reference sample values deviate from the acceptable ranges, see Exhibits D and E for the appropriate action.

8.2.4 If the preparation blank and LCS values are within the acceptable ranges, analyze the spike sample and also the analysis spike sample. If the recovery of any metal deviates from the

acceptable ranges, see Exhibit E for the appropriate action. Proceed to the analysis of samples if the recoveries are acceptable or after consulting Exhibits D and E.

8.2.5 The continuing calibration verification standard (CCV) and the continuing calibration blank (CCB) must be analyzed after every 10 analytical sample analyses. It is required that the analyst run the CCV and CCB after the analysis of the previous sample, but prior to use of a tip wash or other clean out device. CCV concentration values must not deviate from the actual values by more than 10 percent. In addition, the absolute values for the CCB must be lower than the CRQLs. If these conditions are not met at any time during sample analysis, discontinue the analysis and see Exhibits D and E for the appropriate action.

8.2.6 At the end of the sample analysis run, analyze the ICS, CRI, CCV, and CCB. If the values for any of these samples deviates from the required limits, see Exhibits D and E for additional information.

8.3 Sample Analyses

8.3.1 All sample dissolutions must first be analyzed without any dilution. Diluting sample dissolutions is permissible if necessary, provided that the CRQL is not exceeded.

8.3.2 All concentrations within the linear range of the analyte are to be reported. All concentrations reported must be obtained within the established linear range for that analysis run, and interference corrections must be made based on the actual concentration of the interferant and not the apparent concentration obtained when the interferant concentration is above the linear range.

8.4 Calculations

8.4.1 To obtain the analyte concentration (in mg/Kg), multiply the interference corrected analyte values (in mg/L) by the appropriate volume (in liters) used in the fusion and divide by the weight (in Kg) of sample fused.

8.5 Documentation

Report the values in mg/Kg on FORM I-HCIN.

9. Bibliography

9.1 Winge, R.K., V.J. Peterson, and V.A. Fassel, "Inductively Coupled Plasma-Atomic Emission Spectroscopy Prominent Lines", EPA-600/4-79-017.

9.2 Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements", Chemical Analysis, Vol. 46, pp. 41-42.

9.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

9.4 Garbarino, J.R. and Taylor, H.E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing", Applied Spectroscopy 33, No. 3(1979).

9.5 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020.

9.6 Annual Book of ASTM Standards, Part 31.

9.7 "Carcinogens - Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

9.8 "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

9.9 "Safety in Academic Chemistry Laboratories", American Chemical Society Publications, Committee on Chemical Safety, 3rd Edition, 1979.

9.10 "Inductively Coupled Plasma-Atomic Emission Spectrometric Method of Trace Elements Analysis of Water and Waste", Method 200.7 modified by CLP Inorganic Data/Protocol Review Committee; original method by Theodore D. Martin, EMSL/Cincinnati.

Method 200.62-C-CLP

Hydride Generation Inductively Coupled Argon Plasma Optical Emission Spectroscopic Analysis

1. Scope and Application

1.1 This method covers the determination of all concentrations of antimony, arsenic and selenium dissolved by the potassium hydroxide fusion method.

1.2 The method is optimized for selenium, the least sensitive element, which compromises the achievable sensitivities of antimony and arsenic.

1.3 The hydride generation system uses a high sodium borohydride to sample ratio to minimize interferences.

1.4 Many spectral interferences common to the pneumatic nebulization ICP analysis are eliminated.

1.5 Detection limits are lowered generally by a factor of ten over pneumatic nebulization ICP analysis.

2. Summary of Method

2.1 Aliquots of the fusion dissolutions are heated after the addition of an equal volume of concentrated hydrochloric acid. The chloride-chlorine couple developed reduces any selenium (VI) present to the selenium (IV) oxidation state. Selenium must be present in the lower oxidation state to form a hydride.

2.2 In a continuous flow system, the digests are reacted with sodium borohydride, followed by potassium iodide, to produce the volatile hydrides. The iodide-iodine couple reduces any arsenic (V) and antimony (V) to their plus three oxidation states. This circumvents the effect of different hydride formation reaction rates on different oxidation states. The addition of potassium iodide after the addition of the sodium borohydride eliminates the formation of elemental selenium by the iodide-iodine couple.

2.3 The hydrides are stripped from the sample by argon gas and swept into the plasma of an Inductively Coupled Argon Plasma Optical Emission Spectrophotometer. The resulting free atoms are excited into higher electronic states. Atomic and ionic line emission spectra characteristic of the particular metals are produced when the electrons decay back to lower energy levels. The spectra are dispersed by a spectrometer and the intensity of specific line radiation(s) are monitored simultaneously or sequentially by photomultiplier tubes. The photocurrents produced by the photomultiplier tubes will increase in direct proportion to the concentration of the metals in the sample within the linear range of a specific emission line. The photocurrents are processed and controlled by a computer system and related to concentration through a calibration procedure.

2.4 The Method of Standard Additions may be needed to compensate for chemical interferences in the hydride formation reactions.

3. Interferences

3.1 As discussed in Sections 2.1 and 2.2, proper adjustment of the oxidation states of the metals is important in obtaining accurate results.

3.2 Some of the transition metals, especially copper, cause suppression of the hydride formation by reacting to form insoluble salts. Selenium is affected more than the other metals because transition metal selenides are very insoluble. The high acid strength and high sodium borohydride concentration help to temper these effects. The use of the method of standard additions compensates for these effects.

3.3 Spectral interferences common to the pneumatic nebulization analysis of these three metals are eliminated because the interfering metals do not form hydrides and thus are not introduced into the plasma.

4. Apparatus and Equipment

4.1 Computer-controlled inductively coupled argon plasma optical emission spectrometer system with:

4.1.1 Polychromator with associated dispersion and detector system such that the three metals can be determined simultaneously. A fast sequential scanning instrument may be used if the QC requirements set forth in this method can be met.

4.1.2 Radiofrequency generator and coupling system.

4.2 Argon gas supply, welding grade or better.

4.3 Variable speed four channel peristaltic pump and pump tubing.

4.4 Hydride Manifold.

4.5 Phase Separator.

4.6 Screw cap test tubes, 10 mL, with teflon lined caps.

4.7 Water bath or test tube heating block.

4.8 Vortex mixer.

4.9 Assorted laboratory volumetric glassware, pipets and micropipets.

5. Reagents and Standards

5.1 Hydrochloric acid, better than reagent grade.

5.2 Sodium borohydride solution (4.8 percent w/v in 0.25 N NaOH) and potassium iodide solution (8 percent w/v) are prepared from ACS reagent grade chemicals.

5.3 Water equivalent to ASTM Type II is used throughout.

5.4 Stock standard solutions are to be made from ultrapure materials.

5.5 Mixed spiking solutions are made at appropriate concentrations by dilution of the Stock Standard Solution(s). The final solution should contain all three metals at the same concentration in 50 percent v/v HCl. Selenium must be in the plus four oxidation state. To determine the oxidation state of selenium, use the procedure given in Section 5.6.2.

5.6 Calibration Standard Stock Solutions are prepared by dilution of the stock or spiking standard solutions. The final solution must contain all three metals at the same concentration in 50 percent HCl.

5.6.1 The concentration of the metals required in the calibration standard(s) will be dependent upon the instrumentation and so the concentration used as well as the number of standards used is left to the discretion of the analyst, although at least one calibration standard and a calibration blank are required for calibration of the instrument. As a starting point, try calibrating with a mixed standard containing 0.1 mg/L of each of the three metals.

5.6.2 Consideration must be made to assure that selenium is in its plus four oxidation state. Check this by heating one of two portions of the standard(s) in accordance with the procedure given in Section 8.1 and compare the heated versus unheated concentrations obtained. If the heated selenium value is more than five percent higher than the unheated value, some of the selenium is present in the plus six oxidation state. If it is determined that greater than 5 percent of the selenium is present in the higher oxidation state, then all standards must be heated in accordance with the procedure given in Section 8.1.

5.7 Blank Solution, 50 percent (v/v) HCl. This acid must be from the same lot of HCl as that used for the calibration standard stock solution.

5.8 The continuing calibration verification standard is to be made from ultrapure materials. If it is also used as the Initial Calibration Verification, it must be made from a standard of a different source than the calibration standards. If not, it may be the same as one of the calibration standards. The concentrations of the metals are to be at the mid range of the calibration curve. The final solution must contain all three metals at the same concentration in 50 percent (v/v) HCl.

5.9 Rinse Solution, 50 percent (v/v) HCl. The rinse solution must be made from ACS grade or better concentrated HCl.

6. Quality Control

6.1 Instrument Calibration

6.1.1 Summary

Prior to the analysis of samples and required QC, each HYICP system must be initially calibrated to determine instrument sensitivity.

6.1.2 Frequency

Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

6.1.3 Procedure

Calibration standards must be prepared using the same type of matrix and at the same concentration as the preparation blank following sample preparation.

Calibrate according to instrument manufacturers recommended procedures using at least two standards, one being a blank.

6.1.4 Calculations

Not applicable.

6.1.5 Technical Acceptance Criteria

Not applicable.

6.1.6 Corrective Action

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 a CCV and a CCB, respectively.

6.1.7 Documentation

The instrument standardization date and time must be included in the raw data.

6.2 Initial Calibration Verification

6.2.1 Summary

Immediately after the HYICP system has 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) (ICV) at each wavelength used for analysis.

6.2.2 Frequency

Each time the instrument is calibrated, the ICV must be run immediately following the calibration, before any samples are analyzed.

6.2.3 Procedure

If the ICV 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 linear 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.

6.2.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-17}$$

6.2.5 Technical Acceptance Criteria

Recovery for the ICV must be within ± 15 percent of the true value (i.e., 85-115%). (See Table 2, Exhibit C)

6.2.6 Corrective Action

When recoveries of the ICV exceed the technical acceptance criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

6.2.7 Documentation

Report the ICV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.3 Continuing Calibration Verification

6.3.1 Summary

To ensure calibration accuracy during an analysis run, a continuing calibration verification solution (CCV) is analyzed and reported for every wavelength used for the analysis of each analyte.

6.3.2 Frequency

The CCV is run at a frequency of 10 percent or every two hours during an analysis run, whichever is more frequent.

The CCV is also run after the last analytical sample in the analysis run.

6.3.3 Procedure

The same CCV must be used throughout the analysis runs for a Case of samples received.

The analyte concentrations in the continuing calibration standard must be one of the following solutions and should be at or near ± 10 percent the mid-range levels of the calibration curve:

- EPA solutions; or
- A Contractor prepared standard solution.

Each CCV analyzed must reflect the conditions of analysis for all of the 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.

6.3.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-18}$$

6.3.5 Technical Acceptance Criteria

Recovery for the CCV must be within ± 15 percent of the true value (i.e., 85-115%).

6.3.6 Corrective Action

When recoveries of the CCV exceed the technical acceptance criteria, the analysis must be stopped, the problem corrected, the instrument recalibrated, the calibration reverified, and the preceding 10 analytical samples reanalyzed (or all analytical samples since the last "acceptable" CCV analyzed).

6.3.7 Documentation

Report the CCV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.4 CRQL Standard

6.4.1 Summary

To verify linearity near the CRQL, the Contractor must analyze an HYICP standard at two times the CRQL or two times the MDL, whichever is greater. This standard must be run for every wavelength used for analysis.

6.4.2 Frequency

The CRQL standard must be run at the beginning and end of each sample analysis run, or a minimum of twice per eight hours, whichever is more frequent.

6.4.3 Procedure

The CRQL standard is not to be run before the ICV solution.

6.4.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-19}$$

6.4.5 Technical Acceptance Criteria

Recovery of the CRQL standard must be within ± 25 percent of the true value (i.e., 75-125%) for each wavelength used for analysis. (See Table 3, Exhibit C)

6.4.6 Corrective Action

If the CRQL standard does not fall within the control limit, the analysis must be terminated and the problem corrected and the analytical samples since the last acceptable CRQL must be reanalyzed.

6.4.7 Documentation

Report the CRQL standards found concentration, true concentration, and percent recovery on FORM III-HCIN.

6.5 Linear Range Analysis

6.5.1 Summary

The concentration range over which the HYICP calibration curve remains linear must be determined and any values above this linear range, must be diluted and reanalyzed.

6.5.2 Frequency

For all HYICP analyses, a linear range verification check standard (LRS) must be analyzed within 30 days of the start of the contract and at least quarterly (every three calendar months) until the end of the contract. This standard must be run for all wavelengths used for each analyte reported by ICP.

6.5.3 Procedure

The standard must be analyzed 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).

6.5.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-20}$$

6.5.5 Technical Acceptance Criteria

Recovery for the LRS must be within ± 5 percent of the true value (i.e., 95-105%).

6.5.6 Corrective Action

If the recovery of the LRS does not meet the technical acceptance criteria, then the analysis must be terminated and successive dilutions of the standard must be reanalyzed until the control limits are met. The concentration of this standard that meets the control limits is the upper limit of the instrument linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

6.5.7 Documentation

Report the LRS found concentration (in mg/L), true concentration (in mg/L) and percent recovery for each metal on FORM III-HCIN.

6.6 Initial Calibration Blank

6.6.1 Summary

To verify that the HYICP system is not contaminated, an initial calibration blank (ICB) must be analyzed after calibration.

6.6.2 Frequency

The ICB must be analyzed each time the system is calibrated and immediately after the ICV.

6.6.3 Procedure

If the absolute value of the ICB is greater than the MDL, the result must be reported.

6.6.4 Calculations

Not applicable.

6.6.5 Technical Acceptance Criteria

The absolute value of the ICB must be less than the CRQL.

6.6.6 Corrective Action

When the ICB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the ICB.

6.6.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

6.7 Continuing Calibration Blanks

6.7.1 Summary

To ensure that the system is not contaminated during the analysis run, continuing calibration blanks (CCB) are analyzed.

6.7.2 Frequency

Analyze the CCB at a frequency of 10 percent or every two hours, whichever is more frequent.

Analyze the CCB after every CCV.

6.7.3 Procedure

A CCB must be run after the last CCV in the analysis run.

If the absolute value of the CCB is greater than the MDL, the result must be reported.

6.7.4 Calculations

Not applicable.

6.7.5 Technical Acceptance Criteria

The absolute value of the CCB must be less than the CRQL.

6.7.6 Corrective Action

When the CCB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCB analyzed).

6.7.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

6.8 Preparation Blanks

6.8.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

6.8.2 Frequency

At least one PB, must be prepared and analyzed with every SDG, or with each batch[9] of samples digested, whichever is more frequent.

6.8.3 Procedure

The PB shall consist of ASTM Type II water processed through each sample preparation and analysis procedure step (See Exhibit D, Section III).

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.

[9]A group of samples prepared at the same time.

6.8.4 Calculations

Not applicable.

6.8.5 Technical Acceptance Criteria

The absolute value of the PB must be less than the CRQL.

6.8.6 Corrective Action

If the absolute value of the concentration of the blank is less than or equal to the CRQL, no correction of sample results is performed.

If any analyte concentration in the blank is above the CRQL, all associated samples containing less than ten times the blank concentration must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

If an analyte concentration in the blank is below the negative CRQL, then all samples reported below ten times CRQL associated with the blank must be redigested and reanalyzed.

6.8.7 Documentation

The values for the preparation blank must be recorded in mg/Kg on FORM IV-HCIN.

6.9 Spike Sample Analysis

6.9.1 Summary

To provide information about the effect of the sample matrix on the digestion, a known amount of analyte is added (spiked) into a sample.

6.9.2 Frequency

At least one spike sample analysis must be performed on each group of samples of a similar phase for each SDG.[10]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., ICP, HYICP, GFAA, etc.), then the spike samples must be run by each method used.

6.9.3 Procedure

The spike is added before the sample preparation (i.e., prior to fusion, digestion or distillation).

[10] EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

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.

In the instance where there is more than one spike sample per phase 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.

6.9.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-21}$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

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 6.11, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery.

When the sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating percent recovery.

6.9.5 Technical Acceptance Criteria

Recovery for the spike should be within ± 25 percent of the spiked amount (i.e., 75-125%).

6.9.6 Corrective Action

If the spike recovery is not within the limits of 75-125 percent, 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-HCIN and VII-HCIN.

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 percent recovery criteria.

6.9.7 Documentation

Report the spiked sample results, sample results, spike added and percent recovery for the spike sample analysis on FORM VI-HCIN.

The units for reporting spike sample results will be in mg/Kg.

6.10 Analytical Spike Sample Analysis/Method of Standard Additions

6.10.1 Summary

To ensure against bias resulting from interference effects in HYICP analyses, the Method of Standard Additions (MSA) is utilized.

6.10.2 Frequency

All HYICP analyses for each analytical sample will require at least an analytical spike.

The frequency of MSA will depend on the recovery of the analytical spike.

6.10.3 Procedure

All HYICP analyses, including MSA, must fall within the calibration range.

All analyses, except during full MSA require duplicate exposures. Only single exposures are required for MSA quantitation. Average concentration values are used for reporting purposes.

The analytical spike (at 30 percent the linear range) for a sample must be run immediately after that sample. The percent recovery of the analytical spike will determine the method of quantitation for the sample.

An analytical spike is not required for the pre-digestion spike sample.

A maximum of 10 full sample analyses to a maximum of 20 exposures may be performed between each consecutive calibration verifications and blanks. Each full MSA counts as two analytical samples towards determining 10 percent CCV/CCB frequency (i.e., five full MSAs can be performed between calibration verifications).

For analytical runs containing only MSAs, single exposures 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.

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).

MSA spikes must be prepared such that:

a) Spike 1 is approximately 20 percent of the linear range in mg/L;

b) Spike 2 is approximately 40 percent of the linear range in mg/L; and

c) Spike 3 is approximately 60 percent of the linear range in mg/L.

6.10.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-22}$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

6.10.5 Technical Acceptance Criteria

For concentrations ≥ CRQL, the duplicate exposures must agree within ± 20 percent RSD or CV.

The analytical spike recoveries for the LCS and PB MUST be within control limits of ± 15 percent (i.e., MSA is NOT performed on the LCS or PB).

6.10.6 Corrective Action

If the % RSD (CV) technical acceptance criteria are not met, rerun the sample once. If the criteria are still not met, flag the value reported on FORM I-HCIN with the letter "M". **NOTE:** The "M" flag is required for the analytical spike as well as the sample.

If the PB analytical spike technical acceptance criteria are not met, verify the spiking solution by respiking and rerunning the PB once. If the criteria are still not met, correct the problem and reanalyze all analytical samples associated with that blank.

If the LCS analytical spike technical acceptance criteria are not met, correct the problem and reanalyze all analytical samples associated with that LCS.

6.10.7 Documentation

The raw data package must include absorbance and concentration values for both exposures, the average value, and the coefficient of variation (or relative standard deviation, RSD).

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.

Reported values obtained by MSA must be flagged with the letter "S" on FORM I-HCIN if the correlation coefficient is greater than or equal to 0.995. If the correlation coefficient is less than or equal to 0.995, flag the data on FORMs I-HCIN and X-HCIN with a "+". **NOTE:** No combination of these qualifiers can appear in the same field for an analyte.

6.11 Duplicate Sample Analysis

6.11.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods as well as matrix effects.

6.11.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[11]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., HYICP, GFAA, etc.,), then duplicate samples must be run by each method used.

6.11.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per matrix and concentration per method per SDG, if one duplicate result is not within contract criteria, flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculations of relative percent difference.

6.11.4 Calculations

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad \text{D-23}$$

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

Duplicates cannot be averaged for reporting on FORM I-HCIN.

6.11.5 Technical Acceptance Criteria

A control limit of ± 20 percent for RPD shall be used for original and duplicate sample values greater than or equal to five times CRQL (Exhibit C). A control limit of ± the CRQL must be used for sample values less than five times CRQL.

[11]EPA may require additional duplicate sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

If one result is above the five times CRQL level and the other is below, use the ± CRQL criteria.

If both sample values are less than the MDL, the RPD is not calculated.

Specific control limits for each metal will be added to FORM IX-HCIN at a later date based on precision results.

6.11.6 Corrective Action

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk "*".

6.11.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN in mg/Kg.

The absolute value of the control limit (CRQL) must be entered in the "CONTROL LIMIT" column on FORM VIII-HCIN.

6.12 Laboratory Control Samples

6.12.1 Summary

A LCS is digested and analyzed to ensure against analyte loss in the sample preparation.

6.12.2 Frequency

One LCS must be prepared and analyzed for every group of samples in a SDG, or for each batch of samples, whichever is more frequent.

6.12.3 Procedure

The 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 LCS must be obtained from EPA. (If unavailable, other EPA Quality Assurance Check samples or other certified materials may be used.)

6.12.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-24}$$

6.12.5 Technical Acceptance Criteria

Recovery for the LCS must be within ± 20 percent of the true value (i.e., 80-120%).

6.12.6 Corrective Action

If the percent recovery for the LCS falls outside the limit established by EPA, then the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

6.12.7 Documentation

Report the LCS found concentration (in mg/Kg), true concentration (in mg/Kg), and percent recovery on FORM IX-HCIN.

6.13 Method Detection Limits

6.13.1 Summary

The method detection limit (MDL) must be determined before any samples are analyzed for every instrument that will be used.

6.13.2 Frequency

MDLs must be determined within 30 days of the start of the contract and at least quarterly (every three calendar months) until the end of the contract.

6.13.3 Procedure

The Method Detection Limits (in mg/L) shall be determined by multiplying by three, the average of the standard deviations (σ_{n-1}) obtained on three nonconsecutive days from the consecutive analysis of seven different preparation blank dissolutions. 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). MDLs must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined MDL for an instrument must always be used as the MDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the MDL, the MDL for that instrument must be redetermined and the results submitted for use as the established MDL for that instrument for the remainder of the quarter.

MDLs must be determined in mg/L.

6.13.4 Calculations

$$MDL = (\sigma_{n-1}) \times 3 \qquad \text{D-25}$$

6.13.5 Technical Acceptance Criteria

The MDLs must be able to meet the CRQL's established in Exhibit C.

6.13.6 Corrective Action

If an instrument's MDL cannot meet the CRQL for an analyte, that instrument cannot be used to quantitate an analysis unless the analyte concentration is greater than or equal to two times the reported MDL.

6.13.7 Documentation

MDLs must be reported for each instrument used on FORM XI-HCIN submitted with each data package. If multiple instruments are used for the analysis of an analyte within a SDG, the highest MDL for the analyte must be used for reporting concentration values for that SDG.

7. Instrument Operation

7.1 System Configuration

7.1.1 The variable parameters such as incident power, coolant and auxiliary argon flows should be similar to those used for the analysis of water samples with a pneumatic nebulizer. The carrier argon flow and the observation height may have to be changed from that normally used for water samples to obtain the optimum signal for the hydride analyses.

7.1.2 The appropriate cycle times for sampling and rinsing must be determined for each system. These criteria are to be documented and reported in accordance with Exhibits D and E of this contract. Direct monitoring of the photocurrent from the detector system for one of the analytes should be conducted to establish when the signal is at steady state, both for the sample response and in rinsing the sample from the system. Alternatively, sequential exposures of about five to 10 seconds during a cycle can establish the appropriate time intervals. Typically, the sample signal will reach a maximum in 30 to 45 seconds after the sample has entered the phase separator. Rinse times of at least one minute are required between samples. It is required that the contractor document these parameters quarterly in the form of raw data results for this optimization. To test for sample carry-over, the analyst should analyze a high standard (greater than 10 mg/L) containing all the analytes followed by the continuous aspiration of the blank solution. The blank solution is to be continuously monitored (in intensity units) until the intensity becomes stable at the background level. The time required to completely remove all traces of any analyte is the required wash time. If any sample solution analyzed contains any analyte at a concentration greater than the high standard solution analyzed above (prior to dilution correction), the sample following that solution must be reanalyzed. Alternately, the wash check above may be repeated and documented at a higher concentration than the sample.

7.1.3 Every solution, including calibration standards, calibration and method blanks, reference samples, and fused samples, must be analyzed using two full exposures (peak scan) each of which is sufficient to meet the method detection limit for each analyte emission line. All exposure times must be the same for all analyses and all quarterly analyses (i.e., Method Detection Limit, Linear Range, and Interelement Correction Factor).

7.1.4 The phase separator can be easily connected to most instruments by connecting the carrier argon flow to the gas inlet tube of the separator. The gas outlet of the phase separator must contain a glass wool packing and is connected to the nebulizer. The usual sample introduction fitting of the nebulizer will have to be plugged or the connecting tubing pinched shut.

7.1.5 The use of a mass flow controller on the carrier argon flow is recommended in place of a rotometer.

7.1.6 In practice, the carrier argon flow and the sample and reagent flows may have to be adjusted to maintain a stable plasma. The hydride generation reaction evolves a considerable amount of hydrogen, which can destabilize a plasma under normal operating conditions. The flows may be decreased or increased as the analyst sees fit. The ratio of the sample flow to the reagent flows should be maintained.

7.1.7 The flow of the waste line from the phase separator returning to the pump will need to be optimized for each particular system. This is necessary to prevent sample carry-over and must be checked and documented by continuously analyzing a blank solution after a high (greater than 10 mg/L) standard for each element.

7.1.8 The sodium borohydride solution is essentially at saturation and will require stirring with a magnetic stirrer during the analysis.

7.2 System Startup (Recommended)

7.2.1 All pump lines should be pumping only ASTM Type II water.

7.2.2 Set up the instrument with the proper operating parameters as established in Section 7.1. The instrument must be allowed to become thermally stable before beginning the analysis. This requires at least 30 minutes of operation with the plasma lit prior to calibration.

7.2.3 Initiate appropriate operating configuration of the instrument computer.

7.2.4 Perform the appropriate steps recommended by the manufacturer to align the exit slits with the entrance slit.

7.2.5 Place the sample pump line in the acid rinse solution and start the potassium iodide flow.

7.2.6 After the acid has entered the phase separator, start the sodium borohydride flow. Just before the sodium borohydride comes in contact with the rinse solutions, slow the pump down to about half of its normal flow. As soon as the borohydride comes in contact with the acid rinse, a violent reaction starts that evolves hydrogen. Be ready to make adjustments on the flow controls to help stabilize the plasma.

7.2.7 As the plasma stabilizes, slowly increase the flow of the pump to the appropriate level, making adjustments to stabilize the plasma as the amount of hydrogen increases. Hereafter, do not let the sample line remain out of the rinse solution or a digested sample too long. If the borohydride is allowed to build up in the separator without constant acid introduction, the plasma will be extinguished once acid is introduced. If one wants to stop the analysis, place the borohydride line in water and continue pumping the acid until hydrogen evolution ceases. As the hydrogen evolution decreases, adjustments will be needed to stabilize the plasma.

7.3 Linear Range Determination

7.3.1 The linear range of each analyte line must be determined under the same operating conditions used for sample analysis in accordance with Exhibits D and E of this contract. Changes in the operational parameters will change the emission characteristics and will require the re-establishment of the linear range.

7.3.2 The upper limit of the linear range is defined as the highest standard concentration that does not deviate from the calibration curve fit of the lower concentration standards by more than five percent from the known concentration.

7.3.3 All sample values reported shall be based on measurements that are within the linear range of the instrument.

7.4 Method Detection Limit(s) Determination

7.4.1 The method detection limit (MDL) for all metals must be determined using the same operating conditions and/or instrument hardware used for sample analyses and at the frequency required by Exhibits D and E of this contract.

8. Calibration and Sample Analysis

8.1 Sample Preparation

8.1.1 The day that the sample is to be analyzed, transfer 5.0 mL of the fusion dissolution to a 10 mL screw cap test tube. Add 5.0 mL of high purity HCl to the test tube. Volumes for each can be scaled up if 10 mL is found to be inadequate.

8.1.2 Place the cap on the test tube, tighten the cap and mix the solution either on a vortex mixer or by inverting the tube a number of times.

8.1.3 Heat the test tube for 20 minutes at 90 ± 2°C, either in a water bath or block heater.

8.1.4 Cool the solution to room temperature.

8.2 Calibration

8.2.1 Set up the instrument with proper operating parameters as established in Section 7.1. The instrument must be allowed to become thermally stable before beginning analysis. This requires at least 30 minutes of operation with the plasma lit prior to calibration.

8.2.2 Initiate appropriate operating configuration of the computer.

8.2.3 Calibrate the instrument using the appropriate matrix matched calibration standard solution(s). The number of standards utilized is left to the discretion of the operator but must include a calibration blank and at least one standard. The operator should be aware of the requirements in Exhibits D and E that provide for the assurance that all sample values are within the linear range of the initial calibration.

8.2.4 All standards, blanks, and sample solutions must contain 50 percent (v/v) HCl. A change in the acid strength changes the slope of the calibration curve and can cause inaccurate results

8.3 Analysis Sequence

8.3.1 Before beginning the sample analysis run, analyze the initial calibration blank (ICB), initial calibration verification (ICV), and the CRQL standard (CRI) under the same operating conditions intended for sample analyses. The ICV found concentration values must not deviate from the true values by more than 15 percent. The CRI found concentration value must not deviate from the true value by more than 25 percent. The calibration blank values may not exceed the CRQL. If these conditions are not met for any analyte, the analysis shall be discontinued and corrective action applied until the conditions are met (see Exhibits D and E for additional information).

8.3.2 Upon successful analysis of the ICV, and ICB, analyze all method preparation blank (PB) dissolution(s) prepared with the fused samples. If any of the blank(s) values are not less than or equal to the CRQL, see Exhibits D and E for the appropriate action.

8.3.3 If the method blank(s) values are acceptable, analyze the Laboratory Control Sample (LCS). If any LCS values deviate from the acceptable ranges, see Exhibits D and E for the appropriate action.

8.3.4 If the LCS values are within the acceptable ranges, analyze the method spike sample. If the recovery of any element deviates from the acceptable ranges, see Exhibits D and E for the appropriate action. Proceed to the analysis of samples if the recoveries are acceptable or after consulting Exhibit E.

8.3.5 The Continuing Calibration Verification Standard (CCV) and the Continuing Calibration Blank (CCB) must be analyzed after every 10 analytical sample analyses. It is required that the analyst run the CCV and CCB after the analysis of the previous sample, but prior to use of a tip wash or other clean-out device. CCV values must not deviate from the actual values by more than ± 15 percent. In addition, the absolute values for the calibration blank must be lower than the required quantitation limits. If these conditions are not met at any time during samples analysis, discontinue the analysis and see Exhibit E for the appropriate action.

8.3.6 At the end of the sample analysis run, analyze the CRI, CCB and CCV. If the values for any of these samples deviates from the required limits, see Exhibits D and E.

8.4 Sample Analyses

8.4.1 All sample dissolutions must first be analyzed without any dilution. Diluting sample dissolutions is permissible if necessary provided that the CRQL is not exceeded.

8.4.2 All concentrations reported must be obtained within the established linear range for that analysis run. All concentrations within the linear range of the analyte are to be reported. (See Section 7.3)

8.4.3 In order to determine if the sample result is to be calculated by the Method of Standard Addition (MSA), an analytical spike at 30 percent of the instrument's linear range must be performed and analyzed immediately after each sample analysis. The analytical spike recovery must be used to determine the need for MSA as explained in Exhibits D and E. The spiking solution volume must not exceed 10 percent of the sample volume.

8.5 Method of Standard Additions

8.5.1 The following procedure uses a dilution of the sample digest obtained from the procedure described in Section 8.1. A dilution is used so that less than 10 mL of digest will be required for the standard addition set. The dilution is not required but more than 10 mL of sample will have to be digested in the Section 8.1 procedure if the dilution method is not used.

8.5.2 Transfer 2 mL aliquots of the sample digest from Section 8.1 plus 2 mL of the HCl digested blank solution into each of four 10 mL test tubes or sample vials.

8.5.3 To the first aliquot add an appropriate volume of the spiking standard reagent blank solution, mix, and analyze.

8.5.4 Add appropriate volumes of the spiking standard to the remaining three aliquots that result in concentrations at 20 percent, 40 percent and 60 percent of the instruments linear range. The spiking standard solution volume added to each aliquot must not exceed 10 percent of the volume of the aliquot. Add the appropriate amount of blank solution to each aliquot to make the total of spike plus blank volumes added equal.

NOTE: If more than 10 minutes has elapsed since the first aliquot was analyzed, it is suggested, but not required, that the CCV and the CCB be analyzed to determine whether recalibration is required. Performing the calibration verification prior to reanalyzing the first aliquot and the spiked aliquots may save considerable time in the long run, as it can eliminate the repeat analyses required if the CCV or blank values are not within the acceptable limits post sample analysis.

8.5.5 Using a calculator or a statistical package on a computer, determine the slope, the intercepts of the ordinate (y-axis) and the abscissa (x-axis), and the correlation coefficient using the found concentration as the ordinate and the standard addition concentration as the abscissa. The absolute value of the intercept of the abscissa is the concentration of the analyte in the dilute solution. If the correlation coefficient (r) is less than 0.995, then the analyses must be repeated. If the correlation coefficient is stall less than 0.995, report the results on FORM I-HCIN from the run with the best "r" and flag that sample data with a "+".

8.6 Calculations

8.6.1 Determine the method detection limit (MDL) from the standard deviation of the method blank analyte analyses as described in 6.13.

8.6.2 Calculate the method blank(s) concentration (in mg/Kg) by multiplying the value obtained in Section 8.3.2 for the blank by the dilution factors used in Sections 8.4 and 8.5. Assume a 0.25 g weight for the blank.

8.6.3 Calculate sample dissolution concentrations (in mg/L) by multiplying the analyte concentration calculated in Section 8.5 by the appropriate dilution factors used in Sections 8.4 and 8.5. Calculate the sample concentration (in mg/Kg) by multiplying the above result by the dissolution volume (liters) and by dividing by the weight of the fused sample (in Kg). All concentrations are to be reported in units of mg/Kg. No blank subtraction is required.

8.6.4 Calculate all method spike levels relative to the corresponding unspiked sample concentration in units of mg/Kg.

8.6.5 Calculate the relative percent difference (RPD) for both the method and analysis duplicates. Calculate the RPD by dividing the absolute value of the difference between the sample value and the duplicate value by their mean and multiplying by 100.

8.7 Documentation

8.7.1 Record all analyte results on FORM I-HCIN.

Method 202.62-D-CLP

Determination of Potassium Hydroxide Fusion Samples by Graphite Furnace Atomic Absorption (GFAA) Methods Technique

1. Scope and Application

1.1 This method is applicable to the determination of metals dissolved by the potassium hydroxide fusion method (Method 200.62-A-CLP) at all concentrations by Graphite Furnace Atomic Absorption (GFAA) techniques. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account.

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

1.3 Detection limits, sensitivity, and optimum ranges of the metals will vary with the various makes and models of satisfactory graphite furnace atomic absorption spectrometers.

2. Summary of Method

2.1 Using the furnace technique in conjunction with an atomic absorption spectrometer, a representative aliquot of a sample is placed in a graphite tube in the furnace, evaporated to dryness, charred, and atomized. Radiation from a given excited metal is passed through the vapor containing the ground state atoms of that metal. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state metal in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the lamp and a photosensitive device measures the attenuated transmitted radiation.

3. Interferences

3.1 The composition of the sample phase can have a major effect on the analysis. By modifying the sample phase, either to remove interferences or to stabilize the analyte, interferences can be minimized. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium.

3.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. Therefore the use of background correction is required for all furnace analysis.

3.3 Continuum background correction cannot correct for all types of background interference. The use of Zeeman or Smith-Hieftje (or equivalent) background correction is required. When the background interference cannot be compensated for, choose an alternative wavelength, chemically separate the analyte from the interferant, or use an alternative form of background correction.

3.4 Interferences from a smoke producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken to prevent the loss of analyte.

4. Apparatus

4.1 Atomic absorption spectrometer - Single or dual channel, single or double beam instrument having a grating monochrometer, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, background correction, and provisions for interfacing with a recording device.

4.2 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.3 Operating conditions - Because of the differences between various makes and models of satisfactory instruments, no detailed operating conditions 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 on that particular instrument.

4.4 It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements set forth in this SOW and to maintain quality control data confirming instrument performance and analytical results.

5. Reagents and Standards

5.1 Matrix matching, with the samples is mandatory for all blanks, standards, and quality control samples to avoid inaccurate concentration values due to possible standard curve deviations.

5.2 Preparation of standards - Calibration standards are prepared by diluting the stock metal solutions at the time of analysis and are discarded after use. Prepare at least three calibration standards in graduated amounts in the appropriate range by combining an appropriate volume of stock solution in a volumetric flask. All calibration standards must contain 2 g of KOH and 10 mL of concentrated HNO_3 per 100 mL. It is convenient to prepare a solution containing 4 g of KOH and 20 mL of HNO_3 per 100 mL, using 50 mL of this solution per 100 mL in the preparation of the standards.

5.3 Two types of blanks are required for GFAA analysis; the calibration blank is used in establishing the analytical curve while the preparation blank is used to correct for possible contamination resulting from the sample processing. The calibration blank is prepared by diluting 2 g of KOH and 10 mL of HNO_3 to 100 mL with ASTM Type II water. The preparation blank is prepared as specified in section 6.7.3.

6. Quality Control

6.1 Instrument Calibration

6.1.1 Summary

Prior to the analysis of samples and required QC, each GFAA system must be initially calibrated to determine instrument sensitivity.

6.1.2 Frequency

Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

6.1.3 Procedure

Calibration standards must be prepared by diluting the stock solutions at the time of analysis, and are discarded after use.

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.

Calibrate according to instrument manufacturers recommended procedures using at least four standards. Beginning with the calibration blank and working towards the highest standard, run the standards to calibrate. One calibration standard must be a blank, and another must be at the CRQL.

Baseline correction is acceptable as long as it is performed after each and every sample, or after the CCV and CCB, respectively.

Resloping is acceptable as long as it is immediately preceded and immediately followed by a CCV and CCB.

6.1.4 Calculations

Not applicable.

6.1.5 Technical Acceptance Criteria

Not applicable.

6.1.6 Corrective Action

Not applicable.

6.1.7 Documentation

The instrument standardization date and time must be included in the raw data.

6.2 Initial Calibration Verification

6.2.1 Summary

Immediately after the GFAA system has 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) (ICV) at each wavelength used for analysis.

6.2.2 Frequency

Each time the instrument is calibrated, the ICV must be run immediately following the calibration, before any samples are analyzed.

6.2.3 Procedure

If the ICV 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 linear 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.

6.2.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-26}$$

6.2.5 Technical Acceptance Criteria

Recovery for the ICV must be within ± 10 percent of the true value (i.e., 90-110%).

6.2.6 Corrective Action

When recoveries of the ICV exceed the technical acceptance criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

6.2.7 Documentation

Report the ICV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.3 Continuing Calibration Verification

6.3.1 Summary

To ensure calibration accuracy during an analysis run, a continuing calibration verification solution (CCV) is analyzed and reported for every wavelength used for the analysis of each analyte.

6.3.2 Frequency

The CCV is run at a frequency of 10 percent or every two hours during an analysis run, whichever is more frequent.

The CCV is also run after the last analytical sample in the analysis run.

6.3.3 Procedure

The CCV shall contain the analytes at a concentration at or near the mid-range of the calibration curve.

The same CCV must be used throughout the analysis runs for a Case of samples received.

If the CCV 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 linear 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.

Each CCV analyzed must reflect the conditions of analysis for all of the 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.

6.3.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-27}$$

6.3.5 Technical Acceptance Criteria

Recovery for the CCV must be within ± 10 percent of the true value (i.e., 90-110%).

6.3.6 Corrective Action

When recoveries of the CCV exceed the technical acceptance criteria, the analysis must be stopped, the problem corrected, the instrument recalibrated, the calibration reverified, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCV analyzed).

6.3.7 Documentation

Report the CCV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.4 CRQL Standard

6.4.1 Summary

To verify linearity near the CRQL, the Contractor must analyze a GFAA standard at two times the CRQL or two times the MDL, whichever is greater. This standard must be run for every wavelength used for analysis.

6.4.2 Frequency

The CRQL standard must be run at the beginning and end of each sample analysis run, or a minimum of twice per eight hours, whichever is more frequent.

6.4.3 Procedure

The CRQL standard is not to be run before the ICV solution.

6.4.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-28}$$

6.4.5 Technical Acceptance Criteria

Recovery of the CRQL standard must be within ± 25 percent of the true value (i.e., 75-125%) for each wavelength used for analysis. (See Table 3, Exhibit C)

6.4.5 Corrective Action

If the CRQL standard does not fall within the control limit, the analysis must be terminated and the problem corrected and the analytical samples since the last acceptable CRA must be reanalyzed.

6.4.6 Documentation

Report the CRQL standard's found concentration, true concentration, and percent recovery on FORM III-HCIN.

6.5 Initial Calibration Blank

6.5.1 Summary

To verify that the GFAA system is not contaminated, an initial calibration blank (ICB) must be analyzed after calibration.

6.5.2 Frequency

The ICB must be analyzed each time the system is calibrated immediately after the ICV.

6.5.3 Procedure

If the absolute value of the ICB is greater than the MDL, the result must be reported.

6.5.4 Calculations

Not applicable.

6.5.5 Technical Acceptance Criteria

The absolute value of the ICB must be less than the CRQL.

6.5.6 Corrective Action

When the ICB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the ICB.

6.5.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

6.6 Continuing Calibration Blanks

6.6.1 Summary

To ensure that the system is not contaminated during the analysis run, continuing calibration blanks (CCB) are analyzed.

6.6.2 Frequency

Analyze the CCB at a frequency of 10 percent or every two hours, whichever is more frequent.

Analyze the CCB after every CCV.

6.6.3 Procedure

A CCB must be run after the last CCV in the analysis run.

If the absolute value of the CCB is greater than the MDL, the result must be reported.

6.6.4 Calculations

Not applicable.

6.6.5 Technical Acceptance Criteria

The absolute value of the CCB must be less than the CRQL.

6.6.6 Corrective Action

When the CCB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCB analyzed).

6.6.7 Documentation

Report the CCB values in mg/L on FORM IV-HCIN.

6.7 Preparation Blanks

6.7.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

6.7.2 Frequency

At least one PB, must be prepared and analyzed with every SDG, or with each batch[12] of samples digested, whichever is more frequent.

6.7.3 Procedure

The PB shall consist of ASTM Type II water processed through each sample preparation and analysis procedure step (See Exhibit D, Section III).

The first batch of samples in an SDG is to be assigned to PB one, the second batch of samples to PB two, etc.

6.7.4 Calculations

Not applicable.

6.7.5 Technical Acceptance Criteria

The absolute value of the PB must be less than the CRQL.

6.7.6 Corrective Action

If the absolute value of the concentration of the blank is less than or equal to the CRQL, no correction of sample results is performed.

If any analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples must be 10 times the blank concentration. Otherwise, all samples associated with the blank and with the analyte's concentration less than 10 times the blank concentration and above the CRQL, must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

[12] A group of samples prepared at the same time.

If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times CRQL associated with the blank must be redigested and reanalyzed.

6.7.7 Documentation

The values for the PB must be recorded in mg/Kg on FORM IV-HCIN.

6.8 Spike Sample Analysis

6.8.1 Summary

To provide information about the effect of the sample matrix on the digestion, a known amount of analyte is added (spiked) into a sample.

6.8.2 Frequency

At least one spike sample analysis must be performed on each group of samples of a similar phases for each SDG.[13]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., ICP, HYICP, etc.), then spike samples must be run by each method used.

6.8.3 Procedure

The spike is added before the digestion (i.e., prior fusion, distillation or digestion).

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.

In the instance where there is more than one spike sample per phase per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same phase, and method in the SDG.

6.8.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-29}$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

[13] EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

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 6.9, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery.

When the sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating percent recovery.

6.8.5 Technical Acceptance Criteria

Recovery for the spike should be within ± 25 percent of the spiked amount (i.e., 75-125%).

6.8.6 Corrective Action

If the spike recovery is not at or within the limits of 75-125 percent, 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-HCIN and VII-HCIN.

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 percent recovery criteria.

When the digestion spike recovery falls outside the technical acceptance criteria and the sample result does not exceed four times the spike added, a analytical spike must be performed for those metals that do not meet the specified criteria (exceptions: Ag and Hg). Spike an unfortified aliquot of the sample at two times the indigenous level or two times CRQL, whichever is greater.

6.8.7 Documentation

Report the spiked sample results, sample results, spike added and percent recovery for the digestion spike sample analysis on FORM VI-HCIN.

The units for reporting spike sample results will be in mg/Kg.

6.9 Duplicate Sample Analysis

6.9.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods as well as matrix effects.

6.9.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[14]

If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., ICP, HYICP, etc.), then duplicate samples must be run by each method used.

6.9.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per phase per method per SDG, if one duplicate result is not within contract criteria, then flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculation of relative percent difference.

Duplicates cannot be averaged for reporting on FORM I-HCIN.

6.9.4 Calculations

$$\%\ Recovery = \frac{|S - D|}{(S + D)/2} \times 100 \qquad \text{D-30}$$

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

6.9.5 Technical Acceptance Criteria

A control limit of ± 20 percent for RPD shall be used for original and duplicate sample values greater than or equal to five times CRQL (Exhibit C). A control limit of ± the CRQL must be used for sample values less than five times CRQL.

If one result is above the five times CRQL level and the other is below, use the ± CRQL criteria.

For duplicate results < five times CRQL, enter the absolute value of the CRQL in the "CONTROL LIMIT" column of FORM VIII-HCIN.

If both sample values are less than the MDL, the RPD is not calculated.

[14] EPA may require additional duplicate sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

Specific control limits for each metal will be added to FORM VIII-HCIN at a later date based on precision results.

6.9.6 Corrective Action

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk "*".

6.9.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN in mg/Kg.

The absolute value of the control limit (CRQL) must be entered in the "CONTROL LIMIT" column on FORM VIII-HCIN.

6.10 Laboratory Control Samples

6.10.1 Summary

A LCS is digested and analyzed to ensure against analyte loss in the sample preparation.

6.10.2 Frequency

One LCS must be prepared and analyzed for every group of samples in a SDG, or for each batch of samples, whichever is more frequent.

6.10.3 Procedure

The LCS must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received.

If the EPA LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used.

6.10.4 Calculations

$$\% \ Recovery = \frac{Found\ Concntration}{True\ Concentration} \times 100 \qquad \text{D-31}$$

6.10.5 Technical Acceptance Criteria

Recovery for the LCS must be within ± 20 percent of the true value (i.e., 80-120%) with exception of Ag and Sb.

6.10.6 Corrective Action

If the percent recovery for the LCS falls outside the technical acceptance criteria, the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

6.10.7 Documentation

Report the LCS found concentration (in mg/Kg), true concentration (in mg/Kg), and percent recovery on FORM IX-HCIN.

6.11 Analytical Spike Sample Analysis/Method of Standard Additions

6.11.1 Summary

To ensure against bias resulting from interference effects in GFAA analyses, the Method of Standard Additions (MSA) is utilized.

6.11.2 Frequency

All furnace analyses for each analytical sample will require at least one analytical spike.

The frequency of MSA will depend on the recovery of the analytical spike.

6.11.3 Procedure

All furnace analyses, including MSA, must fall within the calibration range.

All analyses, except during full MSA, require duplicate injections. Only single injections are required for MSA quantitation. Average concentration values are used for reporting purposes.

The analytical spike (at a level two times CRQL) of a sample must be run immediately after that sample. The percent recovery of the analytical spike will determine the method of quantitation for the sample.

An analytical spike is not required for the pre-digestion spike sample.

A maximum of 10 full sample analyses to a maximum of 20 injections may be performed between each consecutive calibration verifications and blanks. Each full MSA counts as two analytical samples towards determining 10 percent CCV/CCB frequency (i.e., five full MSAs can be performed between calibration verifications).

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.

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).

MSA spikes must be prepared such that:

a) Spike 1 is approximately 50 percent of the sample concentration in mg/L;

b) Spike 2 is approximately 100 percent of the sample concentration in mg/L; and

c) Spike 3 is approximately 150 percent of the sample concentration in mg/L.

6.11.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-32}$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

$$RSD = \frac{\sigma_{n-1}}{\bar{x}} \qquad \text{D-33}$$

Where:

σ_{n-1} = Standard deviation
X = Mean

6.11.5 Technical Acceptance Criteria

For concentrations greater than or equal to CRQL, the duplicate injections must agree within ± 20 percent of RSD or CV.

The analytical spike recoveries for the LCS and PB MUST be within control limits of ± 15 percent (i.e., MSA is NOT performed on the LCS or PB).

6.11.6 Corrective Action

If the RSD (CV) technical acceptance criteria are not met, rerun the sample once. If the criteria are still not met, flag the value reported on FORM I-HCIN with the letter "M". NOTE: The "M" flag is required for the analytical spike as well as the sample.

If the PB analytical spike technical acceptance criteria are not met, verify the spiking solution by respiking and rerunning the PB once. If the criteria are still not met, correct the problem and reanalyze all analytical samples associated with that blank.

If the LCS analytical spike technical acceptance criteria are not met, correct the problem and reanalyze all analytical samples associated with that LCS.

6.11.7 Documentation

The raw data package must include absorbance and concentration values for both injections, the average value, and the coefficient of variation (or relative standard deviation, RSD).

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.

Reported values obtained by MSA must be flagged with the letter "S" on FORM I-HCIN if the correlation coefficient is greater than or equal to 0.995. If the correlation coefficient is less than or equal to 0.995, flag the data on FORMs I-HCIN and X-HCIN with a "+".

6.12 Method Detection Limits

6.12.1 Summary

The method detection limit (MDL) must be determined before any samples are analyzed for every instrument that will be used.

6.12.2 Frequency

MDLs must be determined within 30 days of the start of the contract and at least quarterly (every three calendar months).

6.12.3 Procedure

The Method Detection Limits (in mg/L) shall be determined by multiplying by three, the average of the standard deviations (σ_{n-1}) obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration three to five times the instrument manufacturer's suggested MDL, 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). MDLs must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined MDL for an instrument must always be used as the MDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the MDL, the MDL for that instrument must be redetermined and the results submitted for use as the established MDL for that instrument for the remainder of the quarter.

MDLs must be determined in mg/L.

6.12.4 Calculations

$$MDL = (\sigma_{n-1}) \times 3 \qquad \text{D-34}$$

Where:

σ_{n-1} = Standard Deviation

6.12.5 Technical Acceptance Criteria

The MDL must be able to meet the CRQL's established in Exhibit C.

6.12.6 Corrective Action

If an instrument's MDL cannot meet the CRQL for an analyte, that instrument cannot be used to quantitate an analysis unless the sample concentration exceeds two times the MDL.

6.12.7 Documentation

MDLs must be reported for each instrument used on FORM XI-HCIN, and must be submitted with each data package. If multiple GFAA instruments are used for the analysis of a metal within a SDG, the highest MDL for the GFAA's must be used for reporting concentration values for that SDG.

7. Instrument Operation

7.1 Instrument Setup

7.1.1 Set up the instrument with the proper operating parameters established by the instrument manufacturer. The individual steps; drying, charring and atomization require careful consideration to ensure each process is carried out effectively. The instrument must be allowed to become thermally stable before beginning any analysis. This usually requires at least 30 minutes of operation prior to calibration. Background correction must be used.

7.2 Calibration and Sample Analysis

7.2.1 Calibrate the instrument according to the manufacturer's recommended procedures and as explained in section 6.1, using calibration standard solutions.

7.2.2 In order to determine if the sample result is to be calculated by MSA, an analytical spike must be performed and analyzed after each sample analysis. The analytical spike recovery must be used to determine the need for MSA as explained in Section 6.11. The spiking solution volume must not exceed 10 percent of the sample volume.

7.2.3 Dilute and reanalyze samples that are more concentrated than the linear range (i.e., top calibration standard) for an analyte.

8. Sample Analysis

8.1 Calibration

8.1.1 Set up the instrument with proper operating parameters as established in Section 7.1. The instrument must be allowed to become thermally stable before beginning analysis. This requires at least 30 minutes of operation with the plasma lit prior to calibration.

8.1.2 Initiate appropriate operating configuration of the computer.

8.1.3 Calibrate the instrument using the appropriate matrix matched calibration standard solution(s). The number of standards utilized is left to the discretion of the analyst but must include a calibration blank and at least three standards. The analyst should be aware of the requirements in Exhibits D and E that provide for the assurance that all sample values are within the linear range of the initial calibration.

8.2 **Analysis Sequence**

8.2.1 Before beginning the sample analysis run, analyze under the same operating conditions intended for sample analyses the initial calibration blank (ICB), initial calibration verifications (ICV), and the CRQL standard (CRI). The ICV found concentration values must not deviate from the true value by more than 10 percent. The CRI found concentration must not deviate from the true value by more than 20 percent. The calibration blank values may not exceed the CRQL. If these conditions are not met for any element, the analysis shall be discontinued and corrective action applied until the conditions are met (see Exhibits D and E for additional information).

8.2.2 Upon successful analysis of the ICV, and ICB, analyze all method preparation blank (PB) dissolution(s) prepared with the fused samples. If any of the blank(s) values are not less than or equal to the CRQL, see Exhibits D and E for the appropriate action.

8.2.3 If the method blank(s) values are acceptable, analyze the Laboratory Control Sample (LCS). If any LCS values deviate from the acceptable ranges, see Exhibits D and E for the appropriate action.

8.2.4 If the LCS values are within the acceptable ranges, analyze the method spike sample. If the recovery of any element deviates from the acceptable ranges, see Exhibits D and E for the appropriate action. Proceed to the analysis of samples if the recoveries are acceptable or after consulting Exhibit E.

8.2.5 The Continuing Calibration Verification Standard (CCV) and the Continuing Calibration Blank (CCB) must be analyzed after every 10 analytical sample analyses. It is required that the analyst run the CCV and CCB after the analysis of the previous sample, but prior to use of any clean-out device. CCV values must not deviate from the actual values by more than ± 10 percent. In addition, the absolute values for the calibration blank must be lower than the required quantitation limits. If these conditions are not met at any time during samples analysis, discontinue the analysis and see Exhibit E for the appropriate action.

8.2.6 At the end of the sample analysis run, analyze the CRA, CCB and CCV. If the values for any of these samples deviates from the required limits, see Exhibits D and E.

8.3 **Sample Analyses**

8.3.1 All sample dissolutions must first be analyzed without any dilution. Diluting sample dissolutions is permissible if necessary provided that the CRQL is not exceeded.

8.3.2 All concentrations reported must be obtained within the established linear range for that analysis run. All concentrations within the linear range of the analyte are to be reported.

8.3.3 In order to determine if the sample result is to be calculated by the Method of Standard Addition (MSA), an analytical spike at two times the CRQL must be performed and analyzed immediately after each sample analysis. The analytical spike recovery must be used to determine the need for MSA as explained in Exhibits D and E. The spiking solution volume must not exceed 10 percent of the sample volume.

8.4 Method of Standard Additions

8.4.1 To the first aliquot add an appropriate volume of the spiking standard reagent blank solution; mix; and analyze.

8.4.2 Add appropriate volumes of the spiking standard to the remaining three aliquots that result in concentrations at 50 percent, 100 percent and 150 percent of the sample concentration. The spiking standard solution volume added to each aliquot must not exceed 10 percent of the volume of the aliquot. Add the appropriate amount of blank solution to each aliquot to make the total of spike plus blank volumes added equal.

8.4.3 Using a calculator or a statistical package on a computer, determine the slope, the intercepts of the ordinate (y-axis) and the abscissa (x-axis), and the correlation coefficient using the found concentration as the ordinate and the standard addition concentration as the abscissa. The absolute value of the intercept of the abscissa is the concentration of the analyte in the dilute solution. If the correlation coefficient (r) is less than 0.995, then the analyses must be repeated. If the correlation coefficient is still less than 0.995, report the results on FORM I-HCIN from the run with the best "r" and flag that sample data with a "+".

8.5 Calculations

8.5.1 Determine the method detection limit (MDL) from the standard deviation of the method blank analyte analyses as described in 6.12.

8.5.2 Calculate the method blank(s) concentration (in mg/Kg) by multiplying the value obtained in Section 8.2.2 for the blank by the dilution factors used in Sections 8.3 and 8.4. Assume a 0.25 g weight for the blank.

8.5.3 Calculate sample dissolution concentrations (in mg/L) by multiplying the analyte concentration calculated in Section 8.4 by the appropriate dilution factors used in Sections 8.3 and 8.4. Calculate the sample concentration (in mg/Kg) by multiplying the above result by the dissolution volume (in liters) and by dividing by the weight of the fused sample (in Kg). All concentrations are to be reported in units of mg/Kg. No blank subtraction is required.

8.5.4 Calculate all method spike levels relative to the corresponding unspiked sample concentration in units of mg/Kg.

8.5.5 Calculate the relative percent difference (RPD) for both the method and analysis duplicates. Calculate the RPD by dividing the absolute value of the difference between the sample value and the duplicate value by their mean and multiplying by 100.

8.6 Documentation

8.6.1 Record all analyte results in mg/Kg on FORM I-HCIN.

THIS PAGE LEFT INTENTIONALLY BLANK

Method 202.2-CLP

Cold Vapor Atomic Absorption (CVAA) Spectroscopic
Determination of Mercury in Industrial Waste Materials

1. Scope and Application

1.1 This method is applicable to the determination of mercury in all industrial waste samples.

1.2 All samples are subject to the same dissolution procedure prior to the measurement of the mercury.

1.3 The method has proven to be accurate for the determination of mercury in standard reference materials consisting of oil, soil, rock, sediment, water, gelatin, and sludge. These materials were quite homogeneous and good precision was obtained.

2. Summary of Method

2.1 Samples of industrial waste materials are phase separated in accordance with Method 50.60-CLP, Section III. Aliquots of the individual phases are digested with a mixture of nitric acid, sulfuric acid, potassium permanganate and potassium persulfate in a sealed reaction vessel for two hours at 95 ± 2°C.

2.2 The mercury in the digests is reduced to the elemental state and carried by nitrogen or air from the solution in a closed system into an optical path where the absorption of radiation at the 253.7 nm wavelength by the mercury vapor is measured. The measured absorbance is related to the concentration of mercury in the sample through the use of a calibration curve.

3. Interferences

3.1 Sulfide interference is removed by the addition of potassium permanganate during sample preparation.

3.2 Volatile organics which absorb at 254 nm are at least partially removed by purging the prepared samples with air or nitrogen before the addition of the reducing agents to the digested samples. In addition, the use of background correction techniques can compensate for such non-atomic absorption. Both flow-through systems and closed loop flow systems (with internal pump) are acceptable. The use of the former is recommended since its relatively sharp mercury peak is more easily distinguished from the broader interference peak. Since many of the samples contain high concentrations of organic species, it is necessary to compensate for this type of interference.

3.3 Chloride present in the sample preparations may be converted to free chlorine during the oxidative digestion process and subsequently absorb radiation at 253.7 nm. To avoid this potential interference, preparations are purged and an excess of hydroxylamine reagent is added prior to mercury reduction.

4. Apparatus and Equipment

4.1 Atomic absorption spectrophotometer - equipped with a cold vapor mercury determination apparatus and a means of carefully monitoring the flow of nitrogen or air purge gas.

4.2 Stripchart recorder.

4.3 Water bath - capable of maintaining a temperature of 95 ± 2°C.

4.4 BOD bottles - 300 mL capacity (or equivalent).

4.5 Nitrogen gas (flow through system) or air recirculation pump with mercury removal system and drying tube.

4.6 Screw top test tubes - 50 mL capacity (25 x 150 mm) (or equivalent).

4.7 Heating block - for test tubes if applicable.

5. **Reagents**

5.1 Sulfuric acid, concentrated - better than reagent grade.

5.1.1 Sulfuric acid, 0.5N - dilute 14.0 mL of concentrated sulfuric acid to one liter with ASTM Type II water.

5.2 Nitric acid, concentrated - better than reagent grade.

5.2.1 Nitric acid, 0.15 percent (v/v) - dilute 1.5 mL of concentrated nitric acid to one liter with ASTM Type II water.

5.3 Stannous chloride solution - add 100 g of stannous chloride to one liter of 0.5 N sulfuric acid.

5.4 Sodium chloride-hydroxylamine hydrochloride solution - dissolve 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride in ASTM Type II water and dilute to one liter.

5.5 Potassium permanganate, 5 percent (w/v) - dissolve 25 g of potassium permanganate in 500 mL ASTM Type II water.

5.6 Potassium persulfate, 5 percent (w/v) - dissolve 25 g of potassium persulfate in 500 mL ASTM Type II water.

5.7 Mercury stock solution, 1000 mg/L - use of NIST traceable commercial standard is acceptable.

5.8 Working mercury solution A, 10.0 mg/L - dilute 1.0 mL of stock mercury solution to 100 mL with 0.15 percent (v/v) nitric acid. This solution should be freshly prepared each time the instrument is calibrated.

5.9 Working mercury solution B, 0.10 mg/L - dilute 1.0 mL of working mercury solution A to 100 mL with 0.15 percent (v/v) nitric acid. This solution should be freshly prepared each time the instrument is calibrated.

6. **Sample Handling and Preservation**

6.1 Once prepared, the mercury preparations should be refrigerated to avoid further degradation of potassium permanganate.

6.2 Because of the extreme sensitivity of the analytical procedure and omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be free of mercury; the samples should not be exposed to any condition in the laboratory that may result in contact to air-borne mercury contamination.

6.3 Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Therefore, when the samples are analyzed, the released mercury vapor should be passed through an absorbing media, such as equal volumes of 0.1 N $KMnO_4$ and 10 percent H_2SO_4 or 0.25 percent iodine in a three percent KI solution. A specially treated charcoal that will absorb mercury vapor is also available.

7. Quality Control

7.1 Instrument Calibration

7.1.1 Summary

Prior to the analysis of samples and required QC, each CVAA system must be initially calibrated to determine instrument sensitivity.

7.1.2 Frequency

Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

7.1.3 Procedure

Calibration standards must be prepared using the same type of matrix and at the same reagent concentration as the preparation blank following sample preparation.

Calibrate according to instrument manufacturers recommended procedures using at least three standards, one being a blank.

7.1.4 Calculations

Not applicable.

7.1.5 Technical Acceptance Criteria

Not applicable.

7.1.6 Corrective Action

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 a CCV and a CCB, respectively.

7.1.7 Documentation

The instrument standardization date and time must be included in the raw data.

7.2 Initial Calibration Verification

7.2.1 Summary

Immediately after the CVAA system has 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) (ICV) at each wavelength used for analysis.

7.2.2 Frequency

Each time the instrument is calibrated, the ICV must be run immediately following the calibration, before any samples are analyzed.

7.2.3 Procedure

If the ICV 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 linear 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.

7.2.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-35}$$

7.2.5 Technical Acceptance Criteria

Recovery for the ICV must be within ± 20 percent of the true value (i.e., 80-120%).

7.2.6 Corrective Action

When recoveries of the ICV exceed the technical acceptance criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

7.2.7 Documentation

Report the ICV found concentration, true concentration, and percent recovery on FORM II-HCIN.

7.3 Continuing Calibration Verification

7.3.1 Summary

To ensure calibration accuracy during an analysis run, a continuing calibration verification solution (CCV) is analyzed and reported for every wavelength used for the analysis of each analyte.

7.3.2 Frequency

The CCV is run at a frequency of 10 percent or every two hours during an analysis run, whichever is more frequent.

The CCV is also run after the last analytical sample in the analysis run.

7.3.3 Procedure

The same CCV must be used throughout the analysis runs for a Case of samples received.

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:

- EPA Solutions; or
- A Contractor prepared standard solution.

Each CCV analyzed must reflect the conditions of analysis for all of the 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.

7.3.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-36}$$

7.3.5 Technical Acceptance Criteria

Recovery for the CCV must be within ± 20 percent of the true value (i.e., 80-120%). (See Table 3, Exhibit C)

7.3.6 Corrective Action

When recoveries of the CCV exceed the technical acceptance criteria, the analysis must be stopped, the problem corrected, the instrument recalibrated, the calibration reverified, and

reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCV analyzed).

7.3.7 Documentation

Report the CCV found concentration, true concentration, and percent recovery on FORM II-HCIN.

7.4 CRQL Standard

7.4.1 Summary

To verify linearity near the CRQL, the Contractor must analyze an CVAA standard at two times the CRQL or two times the MDL, whichever is greater. This standard must be run for every wavelength used for analysis.

7.4.2 Frequency

The CRQL standard must be run at the beginning and end of each sample analysis run, or a minimum of twice per eight hours, whichever is more frequent.

7.4.3 Procedure

The CRQL standard is not to be run before the ICV solution.

7.4.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-37}$$

7.4.5 Technical Acceptance Criteria

The results of the CRQL standard must fall within the control limits of ± 25 percent of the true value (i.e., 75-125%) for each wavelength used for analysis.

7.4.6 Corrective Action

If the CRQL standard does not fall within the control limit, the analysis must be terminated and the problem corrected and the analytical samples since the last acceptable CRQL standard must be reanalyzed.

7.4.7 Documentation

Report the CRQL standards found concentration, true concentration, and percent recovery on FORM III-HCIN.

7.5 Initial Calibration Blank

7.5.1 Summary

To verify that the CVAA system is not contaminated, an initial calibration blank (ICB) must be analyzed after calibration.

7.5.2 Frequency

The ICB must be analyzed each time the system is calibrated and immediately after the ICV.

7.5.3 Procedure

If the absolute value of the ICB is greater than the MDL, the result must be reported.

7.5.4 Calculations

Not applicable.

7.5.5 Technical Acceptance Criteria

The absolute value of the ICB must be less than the CRQL.

7.5.6 Corrective Action

When the ICB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the ICB.

7.5.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

7.6 Continuing Calibration Blanks

7.6.1 Summary

To ensure that the system is not contaminated during the analysis run, continuing calibration blanks (CCB) are analyzed.

7.6.2 Frequency

Analyze the CCB at a frequency of 10 percent or every two hours, whichever is more frequent.

Analyze the CCB after every CCV.

7.6.3 Procedure

A CCB must be run after the last CCV in the analysis run.

If the absolute value of the CCB is greater than the MDL, the result must be reported.

7.6.4 Calculations

Not applicable.

7.6.5 Technical Acceptance Criteria

The absolute value of the CCB must be less than the CRQL.

7.6.6 Corrective Action

When the CCB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCB analyzed).

7.6.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

7.7 Preparation Blanks

7.7.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

7.7.2 Frequency

At least one PB, must be prepared and analyzed with every SDG, or with each batch[15] of samples digested, whichever is more frequent.

7.7.3 Procedure

The PB shall consist of ASTM Type II water processed through each sample preparation and analysis procedure step (See Exhibit D, Section III).

The first batch of samples in an SDG is to be assigned to PB one, the second batch of samples to PB two, etc.

[15]A group of samples prepared at the same time.

7.7.4 Calculations

Not applicable.

7.7.5 Technical Acceptance Criteria

The absolute value of the PB must be less than the CRQL.

7.7.6 Corrective Action

If the absolute value of the concentration of the blank is less than or equal to the CRQL, no correction of sample results is performed.

If any analyte concentration in the blank is above the CRQL, all associated samples containing less than 10 times the blank concentration must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

If an analyte concentration in the blank is below the negative CRQL, then all samples reported below 10 times CRQL associated with the blank must be redigested and reanalyzed.

7.7.7 Documentation

The values for the PB must be recorded in mg/Kg on FORM IV-HCIN.

7.8 Spike Sample Analysis

7.8.1 Summary

To provide information about the effect of the sample matrix on the digestion, a known amount of analyte is added (spiked) into a sample.

7.8.2 Frequency

At least one spike sample analysis must be performed on each group of samples of a similar phases for each SDG.[16]

7.8.3 Procedure

The spike is added before the sample preparation (i.e., prior to fusion, digestion or distillation).

The spiking level shall be equal to the CRQL.

Samples identified as field blanks cannot be used for spiked sample analysis.

[16] EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

EPA may require that a specific sample be used for the spike sample analysis.

In the instance where there is more than one spike sample per phase 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.

7.8.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100 \qquad \text{D-38}$$

Where:
SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

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 7.9, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery.

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating percent recovery.

7.8.5 Technical Acceptance Criteria

Recovery for the spike should be within ± 25 percent of the spiked amount (i.e., 75-125%).

7.8.6 Corrective Action

If the spike recovery is not within the limits of 75-125 percent, 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-HCIN and VII-HCIN.

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 percent recovery criteria.

7.8.7 Documentation

Report the spiked sample results, sample results, spike added and percent recovery for the spike sample analysis on FORM VI-HCIN.

The units for reporting spike sample results will be in mg/Kg.

7.9 Duplicate Sample Analysis

7.9.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods as well as matrix effects.

7.9.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[17]

7.9.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per matrix and concentration per method per SDG, if one duplicate result is not within contract criteria, flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculation of relative percent difference.

7.9.4 Calculations

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

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

Duplicates cannot be averaged for reporting on FORM I-HCIN.

7.9.5 Technical Acceptance Criteria

A control limit of ± 20 percent for RPD shall be used for original and duplicate sample values greater than or equal to five times CRQL (Exhibit C). A control limit of ± the CRQL must be used for sample values less than five times CRQL.

If one result is above the five times CRQL level and the other is below, use the ± CRQL criteria.

---

[17] EPA may require additional duplicate sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

If both sample values are less than the MDL, the RPD is not calculated.

7.9.6 Corrective Action

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk "*".

7.9.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN in mg/Kg.

The absolute value of the control limit (CRQL) must be entered in the "CONTROL LIMIT" column on FORM VIII-HCIN.

7.10 Laboratory Control Samples

7.10.1 Summary

A LCS is digested and analyzed to ensure against analyte loss in the sample preparation.

7.10.2 Frequency

One LCS must be prepared and analyzed for every group of samples in a SDG, or for each batch of samples, whichever is more frequent.

7.10.3 Procedure

The 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 LCS must be obtained from EPA. (If unavailable, other EPA Quality Assurance Check samples or other certified materials may be used.)

7.10.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100$$

7.10.5 Technical Acceptance Criteria

Recovery for the LCS must be within ± 20 percent of the true value (i.e., 80-120%).

7.10.6 Corrective Action

If the percent recovery for the LCS falls outside the technical acceptance criteria, then the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

7.10.7 Documentation

Report the LCS found concentration (in mg/Kg), true concentration (in mg/Kg), and percent recovery on FORM IX-HCIN.

7.11 Method Detection Limits

7.11.1 Summary

The method detection limit (MDL) must be determined before any samples are analyzed for every instrument that will be used.

7.11.2 Frequency

MDLs must be determined within 30 days of the start of the contract and at least quarterly (every three calendar months) until the end of the contract.

7.11.3 Procedure

The MDLs (in mg/L) shall be determined by multiplying by three, the average of the standard deviations (σ_{n-1}) obtained on three nonconsecutive days from the consecutive analysis of seven different PB dissolutions. 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). MDLs must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined MDL for an instrument must always be used as the MDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the MDL, the MDL for that instrument must be redetermined and the results submitted for use as the established MDL for that instrument for the remainder of the quarter.

MDLs must be determined in mg/L.

7.11.4 Calculations

$$MDL = (\sigma_{n-1}) \times 3$$

7.11.5 Technical Acceptance Criteria

The MDLs must be able to meet the CRQLs established in Exhibit C.

7.11.6 Corrective Action

If an instrument's MDL cannot meet the CRQL for an analyte, that instrument cannot be used to quantitate an analysis unless the analyte concentration is greater than or equal to two times the reported MDL.

7.11.7 Documentation

MDLs must be reported for each instrument used on FORM XI-HCIN submitted with each data package. If multiple instruments are used for the analysis of an analyte within a SDG, the highest MDL for the analyte must be used for reporting concentration values for that SDG.

8. Sample Preparation Procedure

8.1 Weigh 0.1 g of analytical sample to the nearest milligram into acid washed screw top test tubes or BOD bottles.

8.2 Add 5.0 mL of concentrated sulfuric acid to each sample and mix. Note if oxidation (bubbling) of the sample occurs. Such samples may react vigorously when the permanganate is added. Then add 2.5 mL of concentrated nitric acid to each sample and mix. Wait 15 minutes.

8.3 Carefully add 50 mL of ASTM Type II water.

8.4 Carefully add 8 mL of 5 percent $KMnO_4$ solution to each sample, mix. After the first permanganate addition, wait until the preparations are not HOT to the touch and add another 16 mL; mix. Wait 15 minutes. If the sample solutions are clear or yellow after 15 minute, add an additional 8 mL of permanganate solution or 0.4 g of solid $KMnO_4$ (depending on available space) to the sample preparation and wait 15 minutes. Repeat this step until the preparations remain purple after the 15 minute wait. If the sample solutions remain purple after the 15 minute wait above, add 8 mL of 5 percent potassium persulfate solution to each sample, cap and mix.

8.5 Place the sample preparations in a pre-heated block heater or water bath at a constant temperature of 95°C for two hours. Remove the samples from the block or bath at the end of the two hours.

NOTE: Tubes have been known to explode when placed under pressure due to weak glass and/or caps. Therefore, it is suggested that preparations be enclosed in a fume hood with the sash down or be surrounded by an explosion shield during heating.

8.6 Check preparations when cooled to see that they remain purple. If clear or yellow, add an additional 8 mL of 5 percent $KMnO_4$ solution or 0.4 g of solid $KMnO_4$ and heat for one hour. Repeat this step until the preparations remain purple after cooling.

8.7 When it is determined that the solution remains purple after cooling, either 8 mL of permanganate solution or 0.4 g of solid permanganate may be added to each preparation.

9. Calibration and Sample Analysis

9.1 Preparation of Calibration Standards for Analysis

9.1.1 If the analytical preparations still have the purple color associated with the $KMnO_4$, proceed to section 9.1.2. If any of the sample preparations are clear or yellow, add either 8.0 mL of 5 percent (w/v) $KMnO_4$ or 0.4 of g solid $KMnO_4$; cap, and heat at 95°C for one hour.

9.1.2 Transfer 2.0 mL (0.2 μg), 5.0 mL (0.5 μg), and 10.0 mL (1.0 μg) of working mercury solution B into separate 300 mL BOD bottles or equivalent.

NOTE: These are recommended standard concentrations and may be changed as long as the required detection limit is maintained and the number of standards is not reduced.

9.1.3 Add 5.0 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid to each standard bottle (not the samples); mix.

9.1.4 Add 16 mL of 5 percent $KMnO_4$ solution to each standard bottle; mix. Allow to cool. Wait 15 minutes.

9.1.5 Add 8 mL 5 percent of $K_2S_2O_8$ solution to each standard bottle; mix.

9.1.6 Add sufficient ASTM Type II water to the standards to attain a total volume of approximately 100 mL in each BOD bottle. The standards are now ready for analysis.

9.2 Sample/Standard Analysis Procedure

9.2.1 Quantitatively transfer the contents of all analytical sample preparations to BOD bottles (if tubes were used) and add sufficient ASTM Type II water to attain a total volume of approximately 100 mL.

9.2.2 First, purge the sample or standard solution in the BOD bottle with nitrogen or air flowing at 1-4 L/min through an aspirator which is stored in a BOD bottle containing ASTM Type II water. During the purge cycle, the purge gas must be vented rather than recirculated. Other purge gas flow rates may be acceptable if consistent with the manufacturer's instructions. Rinse the aspirator thoroughly with ASTM Type II water before returning it to the BOD bottle containing ASTM Type II water.

9.2.3 Next, add 8 mL of hydroxylamine hydrochloride solution to the preparation or standard being analyzed to reduce excess permanganate (solutions may require vigorous swirling to clear the solution).

9.2.4 Wait 30 seconds and add 10 mL of stannous chloride solution to the preparation or standard and immediately place the aspirator into the preparation/standard bottle. Do not agitate the solution. The purge gas flow rate should be set as described above unless the analyst determines that system performance would be optimized at another flow rate. Allow the recorder pen to return to the base line after each deflection and then return the aspirator to the BOD

bottle containing ASTM Type II water for storage prior to the next analysis. Be sure to rinse the aspirator thoroughly with ASTM Type II water prior to replacing the aspirator into the ASTM Type II water storage bottle.

9.3 Standard and Sample Analysis Sequence

9.3.1 Analyze a calibration blank, the lowest concentration calibration standard, the second lowest concentration standard, etc. Scale expansion should be employed if necessary to obtain measurable readings for the blanks. Perform a linear regression analysis of the standards according to Section 10.

9.3.2 Upon successfully analyzing the ICV, analyze the method blank(s). If the obtained blank value(s) exceed the quality control limits, discontinue the analysis and see Exhibit E for appropriate action.

9.3.3 Analyze the samples, the duplicates, and spikes using the flow chart given in Exhibit E to determine the spike sample and also the method spike sample. If the spike percent recovery for mercury deviates from the acceptable ranges, see Exhibit E for appropriate action.

9.4 Preparation Dilution

9.4.1 If a preparation is found to contain mercury in a higher concentration than the highest calibration standard, a new preparation shall be made and diluted prior to analysis. The total volume of the mercury preparation shall be decreased by mixing the preparation vigorously and then pipetting an aliquot of the sample into a BOD bottle (if applicable) and proceeding as per Section 9.2.

NOTE: The solids content of the preparations are quite high and dilution errors may occur if solids are allowed to settle prior to pipetting.

10. Calculations

10.1 Chart recorder peak measurement: Estimate peak heights to the nearest 0.5 mm for peak heights under 5 mm or to the nearest mm for higher values. Instrument scale changes or recorder range adjustments to instruments should be made when necessary to make measurements of otherwise off-scale peaks. When using a chart recorder in conjunction with an integrator, the area calculated by the integrator may be used in lieu of the peak height measurement.

10.2 Construct a calibration solution response curve by using a linear least squares treatment (regression analysis) of the standard peak height or absorbance (y) as a function of mass in μg (x). A correlation coefficient of greater than or equal to 0.995 is required. If this is not achieved, the analysis must be repeated after the problem is corrected. Report the correlation coefficient, slope, and y intercept on the strip chart (see Exhibit B).

10.2.1 The mercury contained in a sample (in μg) is found by entering the peak height or absorbance into the regression equation and obtaining equivalent μg of mercury. The recorder or instrument range setting must be taken into account during the calculation.

10.2.2 The sample concentration of mercury in units of $\mu g/g$ is found by dividing the mass of mercury in μg, (found from the regression analysis) by the exact weight of the aliquot (in g) used in the sample preparation. If the sample was diluted prior to analysis, multiply the $\mu g/g$ value times the dilution factor used. Report values down to the required MDL (0.3 $\mu g/g$) or to 10x the obtained method blank value, as described in Section 7. Record sample results on the appropriate form in Exhibit B.

NOTE: $\mu g/g$ is proportional to mg/Kg.

11. Documentation

11.1 Report all mercury values in mg/Kg on FORM I-HCIN.

THIS PAGE LEFT INTENTIONALLY BLANK

Method 335.63-CLP

Colorimetric Determination of Cyanide
in Industrial Waste Materials

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 in all phases by distillation. Either a manual or automated colorimetric analysis of the distillate may be utilized.

1.3 The detection limit for the automated colorimetric option of this method is approximately 0.5 $\mu g/g$ CN^- and for the manual colorimetric option it is approximately 1.5 $\mu g/g$. The reporting limit for both methods is 1.5 $\mu g/g$.

1.4 The presence of cyanide as determined by this method does not in itself characterize the waste as a RCRA Reactivity Hazardous Waste.

2. Summary of Method

2.1 Cyanide is released from most of its complexes and converted to hydrogen cyanide by means of a reflux distillation. The hydrogen cyanide gas is drawn by vacuum into a solution of sodium hydroxide where it is absorbed as sodium cyanide.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride by reaction with chloramine-T at a pH less than 8 without hydrolysis to cyanate. After the reaction is complete, color is formed on the addition of pyridine barbituric acid reagent and the absorbance of the color 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. Apparatus

3.1 Reflux distillation apparatus as shown in Figures 1 and 2.

3.2 Heating block - capable of maintaining a temperature of 125 ± 5°C.

3.3 Autoanalyzer system or spectrophotometer (580 nm) with accessories:

3.3.1 Sampler

3.3.2 Pump

3.3.3 Cyanide cartridge

3.3.4 Colorimetric with 50 mm flowcells and 570 or 580 nm filters

3.3.5 Chart recorder

3.4 Assorted volumetric glassware, pipets, and micropipets.

4. Reagents and Standards (Reagent grade unless otherwise specified)

4.1 Sodium hydroxide absorbing solution, and sample wash solution, 0.25 N - dissolve 10.0 g NaOH in ASTM Type II water and dilute to 1 L.

4.2 Sodium hydroxide developing solution, 0.05 N - dissolve 2.0 g NaOH in ASTM Type II water and dilute to 1 L. (Manual Colorimetric Method.)

4.3 Sodium hydroxide solution, 0.1 N - dissolve 4 g of NaOH in ASTM Type II water and dilute to 1 L.

4.4 Sodium hydroxide solution, 1.25 N - dissolve 50 g of NaOH in ASTM Type II water and dilute to 1 L.

4.5 Magnesium chloride solution, 51 percent (w/v) - dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in ASTM Type II water and dilute to 1 L.

4.6 Sulfuric acid, 50 percent (v/v) - carefully add a portion of concentrated H_2SO_4 to an equal portion of ASTM Type II water.

4.7 Stock cyanide solution, 1000 mg/L CN^- - dissolve 2.51 g of KCN and 2.0 g of KOH in ASTM Type II water and dilute to 1 L. Standardize in accordance with Section 7.1.

4.8 Intermediate cyanide standard solution, 10 mg/L CN^- - dilute 1.0 mL of the stock cyanide solution plus 20 mL of 1.25 N NaOH solution to 100 mL with ASTM Type II water. Prepare this solution at time of analysis.

4.9 Rhodanine indicator - dissolve 20 mg of p-dimethylamino-benzal-rhodanine in 100 mL of acetone.

4.10 Silver nitrate solution, 0.0192 N - prepare by crushing approximately 5 g of $AgNO_3$ crystals and drying to constant weight at 104°C. Weigh out 3.2647 g of dried $AgNO_3$ and dissolve in ASTM Type II water. Dilute to 1 L (1 mL corresponds to 1 mg CN^-).

4.11 Potassium chromate indicator solution - dissolve 50 g of K_2CR0_4 in sufficient ASTM Type II water. Add silver nitrate solution until a definite red precipitate is formed. Let stand at least 12 hours, filter, and dilute to 1 L with ASTM Type II water.

4.12 Primary standard sodium chloride, 0.0141 N - dissolve 824.1 mg of NaCl (NIST-dried 20 minutes at 104°C) in ASTM Type II water and dilute to 1 L.

4.13 Phosphate buffer solution, 1 M - dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in ASTM Type II water and dilute to 1 L. Filter before use and store at 4 ± 2°C.

4.14 Chloramine-T solution, 0.4 percent (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. (Automated Colorimetric Method.)

4.15 Chloramine-T solution, 1 percent (w/v) - dissolve 1.0 g of chloramine-T in 100 mL ASTM Type II water. Prepare fresh at time of analysis. (Manual Colorimetric Method.)

4.16 Pyridine barbituric acid color reagent solution - prepare this solution in the hood. Transfer 15 g of barbituric acid into a 1 L 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 of concentrated HCl and mix until all of the barbituric acid is dissolved. Dilute to 1 L with ASTM Type II water. Store at 4 ± 2°C.

5. Sample Handling and Preservation

5.1 Exposure of sample to air may cause oxidation of samples.

5.2 If the cyanide sample is a liquid phase and also suspected of containing oxidants, $Na_2S_2O_3$ must be added to prevent further oxidation of the sample. (See Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985.)

5.3 Cyanide samples containing 100 percent water miscible phase liquids with no centrifugable solids will be pretreated with cadmium nitrate $Cd(NO_3)_2$, and centrifuged to remove soluble sulfides. Do not attempt to remove sulfides from samples containing solids, as the centrifugation will remove sample. Other phase types containing sulfides will be distilled using a two trap system where the first trap contains a lead acetate solution (see Method 376.63-CLP) to trap the sulfide and the second trap contains sodium hydroxide to trap the cyanide. (See Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985).

6. Quality Control

6.1 Instrument Calibration

6.1.1 Summary

Prior to the analysis of samples and required QC, each system must be initially calibrated to determine instrument sensitivity.

6.1.2 Frequency

Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

6.1.3 Procedure

Calibration standards must be prepared using the same type of matrix and at the same reagent concentration as the preparation blank following sample preparation.

Calibrate according to instrument manufacturers recommended procedures using at least two standards, one being a blank.

6.1.4 Calculations

Not applicable.

6.1.5 Technical Acceptance Criteria

Not applicable.

6.1.6 Corrective Action

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 a CCV and a CCB, respectively.

6.1.7 Documentation

The instrument standardization date and time must be included in the raw data.

6.2 Initial Calibration Verification

6.2.1 Summary

Immediately after the system has 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) (ICV) at each wavelength used for analysis.

6.2.2 Frequency

Each time the instrument is calibrated, the ICV must be run immediately following the calibration, before any samples are analyzed.

6.2.3 Procedure

If the ICV 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 linear 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.

6.2.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-42}$$

6.2.5 Technical Acceptance Criteria

Recovery for the ICV must be within ± 15 percent of the true value (i.e., 85-115%). (See Table 3, Exhibit C)

6.2.6 Corrective Action

When recoveries of the ICV exceed the technical acceptance criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

6.2.7 Documentation

Report the ICV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.3 Continuing Calibration Verification

6.3.1 Summary

To ensure calibration accuracy during an analysis run, a continuing calibration verification solution (CCV) is analyzed and reported for every wavelength used for the analysis of each analyte.

6.3.2 Frequency

The CCV is run at a frequency of 10 percent or every two hours during an analysis run, whichever is more frequent.

The CCV is also run after the last analytical sample in the analysis run.

6.3.3 Procedure

The same CCV must be used throughout the analysis runs for a Case of samples received.

The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near ± 10 percent the mid-range levels of the calibration curve:

- EPA Solutions; or
- A Contractor prepared standard solution.

Each CCV analyzed must reflect the conditions of analysis for all of the 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.

6.3.4 Calculations

$$\%\ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-43}$$

6.3.5 Technical Acceptance Criteria

Recovery for the CCV must be within ± 15 percent of the true value (i.e., 85-115%).

6.3.6 Corrective Action

When recoveries of the CCV exceed the technical acceptance criteria, the analysis must be stopped, the problem corrected, the instrument recalibrated, the calibration reverified, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCV analyzed).

6.3.7 Documentation

Report the CCV found concentration, true concentration, and percent recovery on FORM II-HCIN.

6.4 CRQL Standard

6.4.1 Summary

To verify linearity near the CRQL, the Contractor must analyze a standard at two times the CRQL or two times the MDL, whichever is greater. This standard must be run for every wavelength used for analysis.

6.4.2 Frequency

The CRQL standard must be run at the beginning and end of each sample analysis run, or a minimum of twice per eight hours, whichever is more frequent.

6.4.3 Procedure

The CRQL standard is not to be run before the ICV solution.

6.4.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-44}$$

6.4.5 Technical Acceptance Criteria

The results of the CRQL standard must fall within the control limits ± 25 percent of the true value for each wavelength used for analysis.

6.4.6 Corrective Action

If the CRQL standard does not fall within the control limit, the analysis must be terminated and the problem corrected and the analytical samples since the last acceptable CRQL standard must be reanalyzed.

6.4.7 Documentation

Report the CRQL standards found concentration, true concentration, and percent recovery on FORM III-HCIN.

6.5 Initial Calibration Blank

6.5.1 Summary

To verify that the system is not contaminated, an initial calibration blank (ICB) must be analyzed after calibration.

6.5.2 Frequency

The ICB must be analyzed each time the system is calibrated and immediately after the ICV.

6.5.3 Procedure

If the absolute value of the ICB is greater than the MDL, the result must be reported.

6.5.4 Calculations

Not applicable.

6.5.5 Technical Acceptance Criteria

The absolute value of the ICB must be less than the CRQL.

6.5.6 Corrective Action

When the ICB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the ICB.

6.5.7 Documentation

Report the ICB values in mg/L on FORM IV-HCIN.

6.6 Continuing Calibration Blanks

6.6.1 Summary

To ensure that the system is not contaminated during the analysis run, continuing calibration blanks (CCB) are analyzed.

6.6.2 Frequency

Analyze the CCB at a frequency of 10 percent or every two hours, whichever is more frequent.

Analyze the CCB after every CCV.

6.6.3 Procedure

A CCB must be run after the last CCV in the analysis run.

If the absolute value of the CCB is greater than the MDL, the result must be reported.

6.6.4 Calculations

Not applicable.

6.6.5 Technical Acceptance Criteria

The absolute value of the CCB must be less than the CRQL.

6.6.6 Corrective Action

When the CCB concentration does not meet the technical acceptance criteria, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples (or all analytical samples since the last "acceptable" CCB analyzed).

6.6.7 Documentation

Report the CCB values in mg/L on FORM IV-HCIN.

6.7 Preparation Blanks

6.7.1 Summary

To ensure against contamination during sample preparation, a preparation blank (PB) is analyzed.

6.7.2 Frequency

At least one PB, must be prepared and analyzed with every SDG, or with each batch[18] of samples digested, whichever is more frequent.

6.7.3 Procedure

The PB shall consist of ASTM Type II water processed through each sample preparation and analysis procedure step (See Exhibit D, Section III).

The first batch of samples in an SDG is to be assigned to PB one, the second batch of samples to PB two, etc.

[18]A group of samples prepared at the same time.

6.7.4 Calculations

Not applicable.

6.7.5 Technical Acceptance Criteria

The absolute value of the PB must be less than the CRQL.

6.7.6 Corrective Action

If the absolute value of the concentration of the blank is less than or equal to the CRQL, no correction of sample results is performed.

If any analyte concentration in the blank is above the CRQL, all associated samples containing less than 10 times the blank concentration must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

If an analyte concentration in the blank is below the negative CRQL, then all samples reported below 10 times CRQL associated with the blank must be redigested and reanalyzed.

6.7.7 Documentation

The values for the PB must be recorded in mg/Kg on FORM IV-HCIN.

6.8 Spike Sample Analysis

6.8.1 Summary

To provide information about the effect of the sample matrix on the distillation, a known amount of analyte is added (spiked) into a sample.

6.8.2 Frequency

At least one spike sample analysis must be performed on each group of samples of a similar phases for each SDG[19]

If two analytical methods are used to obtain the reported values for the same analyte within a SDG, then spike samples must be run by each method used.

6.8.3 Procedure

The spike is added before the sample preparation and prior to analysis.

Samples identified as field blanks cannot be used for spiked sample analysis.

[19] EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

EPA may require that a specific sample be used for the spike sample analysis.

The spike must be at a concentration equal to 30 percent of the analytes linear range.

In the instance where there is more than one spike sample per phase 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.

6.8.4 Calculations

$$\% \ Recovery = \frac{(SSR - SR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

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 6.9, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery.

When sample concentration is less than the method detection limit, use SR = 0 only for purposes of calculating percent recovery.

6.8.5 Technical Acceptance Criteria

Recovery for the analytical spike should be within ± 25 percent of the spiked amount (i.e., 75-125%).

6.8.6 Corrective Action

If the spike recovery is not at or within the limits of 75-125 percent, 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-HCIN and VI-HCIN.

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 percent recovery criteria.

When the digestion spike recovery falls outside the technical acceptance criteria and the sample result does not exceed four times the spike added, a analytical spike must be performed. Spike the unspiked aliquot of the sample at two times the indigenous level or two times CRQL, whichever is greater.

6.8.7 Documentation

Report the spiked sample results, sample results, spike added and percent recovery for the spike sample analysis on FORM VI-HCIN.

The units for reporting spike sample results will be in mg/Kg.

6.9 Duplicate Sample Analysis

6.9.1 Summary

Duplicate aliquots of a sample are carried through the preparation and analysis steps to provide information about the precision of the analytical methods as well as matrix effects.

6.9.2 Frequency

At least one duplicate sample analysis must be performed on each group of samples of a similar phase for each SDG.[20]

If two analytical methods are used to obtain the reported values for the same metal within a SDG, then duplicate samples must be run by each method used.

6.9.3 Procedure

Samples identified as field blanks cannot be used for duplicate sample analysis.

EPA may require that a specific sample be used for the duplicate sample analysis.

In the instance where there is more than one duplicate sample per matrix and concentration per method per SDG, if one duplicate result is not within contract criteria, flag all the samples of the same phase and method in the SDG.

Duplicate sample analyses are required for calculations of relative percent difference.

6.9.4 Calculations

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

Where:

RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate).

Duplicates cannot be averaged for reporting on FORM I-HCIN.

[20] EPA may require additional duplicate sample analysis upon special request by the Project Officer for which the Contractor will be paid.

6.9.5 Technical Acceptance Criteria

A control limit of ± 20 percent for RPD shall be used for original and duplicate sample values greater than or equal to five times CRQL (Exhibit C). A control limit of ± the CRQL must be used for sample values less than five times CRQL.

If one result is above the five times CRQL level and the other is below, use the ± CRQL criteria.

If both sample values are less than the MDL, the RPD is not calculated.

Specific control limits for each element will be added to FORM IX-HCIN at a later date based on precision results.

6.9.6 Corrective Action

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk "*".

6.9.7 Documentation

The results of the duplicate sample analyses must be reported on FORM VIII-HCIN in mg/Kg.

The absolute value of the control limit (CRQL) must be entered in the "CONTROL LIMIT" column on FORM VIII-HCIN.

6.10 Laboratory Control Samples

6.10.1 Summary

A LCS is digested and analyzed to ensure against analyte loss in the sample preparation.

6.10.2 Frequency

One LCS must be prepared and analyzed for every group of samples in a SDG, or for each batch of samples, whichever is more frequent.

6.10.3 Procedure

The 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 LCS must be obtained from EPA. (If unavailable, other EPA Quality Assurance check samples or other certified materials may be used.)

6.10.4 Calculations

$$\% \ Recovery = \frac{Found\ Concentration}{True\ Concentration} \times 100 \qquad \text{D-47}$$

6.10.5 Technical Acceptance Criteria

Recovery for the LCS must be within ± 20 percent of the true value (i.e., 80-120%).

6.10.6 Corrective Action

If the percent recovery for the LCS falls outside the technical acceptance criteria, then the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

6.10.7 Documentation

Report the LCS found concentration (in mg/Kg), true concentration (in mg/Kg), and percent recovery on FORM IX-HCIN.

6.11 Method Detection Limits

6.11.1 Summary

The method detection limit (MDL) must be determined before any samples are analyzed for every instrument that will be used.

6.11.2 Frequency

MDLs must be determined within 30 days of the start of the contract and at least quarterly (every three calendar months) until the end of the contract.

6.11.3 Procedure

The MDL (in mg/L) shall be determined by multiplying by three, the average of the standard deviations (σ_{n-1}) obtained on three nonconsecutive days from the consecutive analysis of seven different preparation blank dissolutions. 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). MDLs must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined MDL for an instrument must always be used as the MDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the MDL, the MDL for that instrument must be redetermined and the results submitted for use as the established MDL for that instrument for the remainder of the quarter.

MDLs must be determined in mg/L.

6.11.4 Calculations

$$MDL = (\sigma_{n-1}) \times 3$$ D-48

6.11.5 Technical Acceptance Criteria

The MDL's must be able to meet the CRQL's established in Exhibit C.

6.11.6 Corrective Action

If an instrument's MDL cannot meet the CRQL for an analyte, that instrument cannot be used to quantitate an analysis unless the analyte concentration is greater than or equal to two times the reported MDL.

6.11.7 Documentation

MDLs must be reported for each instrument used on FORM XI-HCIN submitted with each data package. If multiple instruments are used for the analysis of an analyte within a SDG, the highest MDL for the analyte must be used for reporting concentration values for that SDG.

7. Sample Preparation

7.1 The procedure described here utilizes a midi distillation apparatus (see Figure 1) and requires a sample aliquot of one gram or less. Alternatively, the distillation apparatus pictured in Figure 2 may be used along with the procedure described for soils and sludges in the appendix to ASTM Method D-2036, Volume 11.02, 1983.

7.2 Weigh 1.0 g of analytical sample to the nearest 0.01 g into the reaction vessel and add 10 mL of 0.25 N NaOH and 0.5 mL of $MgCl_2 \cdot 6H_2O$ solution to each reaction vessel. For sample weights less than one gram, weigh the sample to three significant figures. (It is recommended that the analyst pre-fit the distillation head to the reaction vessel prior to weighing the sample into the reaction vessel since the glassware may vary in size.)

7.3 Add 50 mL of 0.25 N NaOH to the receiving vessels and insert fritted impingers.

7.4 Connect the apparatus as shown in Figure 1. The excess cyanide trap contains 0.5 N NaOH.

7.5 Turn on the vacuum and adjust the gang valves to give a flow of three bubbles per second from the impingers in each reaction vessel. Seal all fittings with ASTM Type II water.

7.6 After five minutes of vacuum flow, inject 1.0 mL of 50 percent (v/v) H_2SO_4 through the top part of the distillation head into the reaction vessel. After addition of the H_2SO_4, the solution should become clear of the $Mg(OH)_2$. If not, sufficient acid may not have been added.

NOTE: Steps should be taken prior to distillation to assure that the necessary acid volume is added to the sample to bring the sample/solution pH to below 2.0.

7.7 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 rate. (Impinger may occasionally plug.)

7.8 After two hours of refluxing, turn off the heating block and continue the vacuum for an additional 15 minutes.

7.9 Seal the receiving solutions and store them at 4 ± 2°C until analyzed. The solutions will be stable for up to a week.

7.10 If the distillation fails to work properly due to formation of soaps, liquid carryover, etc., steps must be taken to eliminate these problems. Possible alternatives include use of a smaller sample aliquot or an additional receiving vessel in train (all other alternatives must be approved by the Administrative or Technical Project Officer). In the latter, a receiving vessel containing ASTM Type II water acidified to a pH less than 2.0 would be inserted between the existing reaction and receiving vessels.

8. Calibration, Standardization, and Sample Analysis

8.1 Stock Cyanide Solution Standardization

8.1.1 Fill a 10 mL microburet with the 0.0192 N $AgNO_3$ solution.

8.1.2 Pipet 10.0 mL of ASTM Type II water into a well-washed Erlenmeyer flask. Adjust the pH of the water to between 7.0 and 10.0 with NaOH or H_2SO_4. Add 1.0 mL of the K_2Cr0_4 indicator solution. Titrate with the $AgNO_3$ to a pinkish yellow end point. Be consistent in end point recognition. Record the mL of titrant used. Titrate three blanks and average the volume of titrant used; this is equal to A.

8.1.3 Titrate three individual 10.0 mL aliquots of the standard 0.0141 N NaCl solution in the same manner as the blanks. Average the mL of titrant used; this is equal to B.

8.1.4 Calculate the exact normality of the $AgNO_3$ solution:

$$N_{AgNO_3} = \frac{me\ NaCl\ mL}{(B - A)\ mL} \times 0.0141\ N \qquad \text{D-49}$$

8.1.5 Add 10.0 mL of ASTM Type II water to a well-washed Erlenmeyer flask. Add 100 mL of 0.1 N NaOH and 0.5 mL of the rhodanine indicator solution. Titrate with the standard $AgNO_3$ titrant to the first change in color from a canary yellow to a salmon hue. Record the volume of titrant used. Titrate three blanks and calculate the average volume of titrant used (this is equal to C).

8.1.6 Titrate three individual 10.0 mL aliquots of the stock cyanide solution in the same manner as the blanks. Calculate the average volume of titrant used (this is equal to D).

8.1.7 Calculate the concentration of cyanide in the stock solution:

$$mg/L\ CN^- = \frac{(D - C)\ (N\ AgNO_3)}{mL\ stock\ CN^-} \times \frac{2\ eq\ CN^-}{1\ eq\ Ag^+} \times \frac{26\ mg\ CN^-}{Meq} \times \frac{1000\ mL}{L} \qquad \text{D-50}$$

8.2 **Automated Colorimetric Calibration and Analysis**

8.2.1 Prepare standard cyanide solutions according to the table in 8.3.3.

8.2.2 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.

8.2.3 The following general procedure applies to the automated method for cyanide: Set up the manifold and complete system as per manufacturer's instructions. Let the colorimeter and recorder warm up for at least 30 minutes. Establish a steady reagent baseline feeding ASTM Type II water through the sample line and the appropriate reagents through the reagent lines. Adjust the baseline using the appropriate control on the colorimeter.

8.2.4 Aspirate the highest calibration standard and adjust the colorimeter until the desired single-range is obtained.

8.2.5 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates and all distilled QC audit samples.

8.2.6 Switch sample line from the ASTM Type II water to sampler, set the appropriate sample rate and begin analysis.

8.3 **Manual Colorimetric Calibration and Analysis**

8.3.1 Turn on the spectrophotometer and allow appropriate warm-up time.

8.3.2 Using an opaque object, block the light path in the spectrophotometer and set the absorbance to full scale (zero transmittance). Set the absorbance to zero by placing a calibration blank (see below) in the light path. Do not repeat the zeroing with the blank prior to each sample analysis.

8.3.3 Prepare a set of standards in 50 mL volumetric flasks using the following protocol:

Total μg CN^- / standard solution	mL 10 mg/L CN^-	mL 0.05 N NaOH*
0.00	0.000	20
0.20	0.020	20
0.50	0.050	20
1.00	0.100	20
2.00	0.200	20
5.00	0.500	20

* Addition of 20 mL of NaOH to each sample will result in a 2.5 percent difference in NaOH concentration between the blank and the highest CN^- standard. This should not appreciably affect standard calibration.

8.3.4 Add 4 mL phosphate buffer to each of the standard solutions prepared above and mix.

8.3.5 Using the Time Table for Manual Color Development found below, add the following reagents to each solution in the order given: 2.0 mL of chloramine-T solution, swirl to mix; after 15 seconds add 5.0 mL of pyridine barbituric acid solution, swirl gently to mix; dilute calibration standard to 50 mL using ASTM Type II water after four minutes.

8.3.6 Measure absorbance or transmittance of calibration standards.

Time Table for Manual Color Development
(Time is in minutes:seconds)

Sample No.	Chlor-T	Absorbance Pyridine	Dilution	Reading
1	0:00	0:15	4:15	13:00
2	0:45	1:00	5:00	13:45
3	1:30	1:45	5:45	14:30
4	2:15	2:30	6:30	15:15
5	3:00	3:15	7:15	16:00
6	3:45	4:00	8:00	16:45

8.3.7 Repeat sections 8.3.4-8.3.5 using 4 mL of sample from the receiving vessel solution diluted to 20 mL total volume with ASTM Type II water (in place of the standard solutions). A blank and one of the mid-range standards will be developed and analyzed with each manual color development of sample solutions. If any sample solution absorbance reads above the highest calibration standard, repeat the color development using an appropriate volume of sample receiving solution to bring the absorbance value below the highest calibration standard. Be sure to keep salt content constant in the development solutions. The mid-range standards will serve as the calibration stability standard.

9. Calculations

9.1 Calculations for Automated Colorimetric Determination

9.1.1 Perform a linear regression analysis of the calibration standards values (µg/mL) (x) versus absorbance values (y) to determine the correlation. If the correlation coefficient is less than 0.995, then the calibration curve analysis should be repeated using new standards if necessary.

9.1.2 Using the regression analysis equation, calculate sample receiving solution concentrations (as µg/mL) from the calibration curve.

9.1.3 Calculate µg/g, CN^-, for the samples using the following equation:

$$\mu g/g,\ CN^- = \frac{(A \times B \times C)}{sample\ wt.\ in\ g} \qquad \text{D-51}$$

Where:

A = µg/mL from regression analysis;
B = Sample receiving solution volume (mL); and
C = Dilution factor necessary to bracket sample value within standard values.

9.1.4 Report all sample values greater than the required reporting limit except as noted in Exhibit E.

9.2 Calculations for Manual Colorimetric Determination

9.2.1 Perform a linear regression analysis of the calibration standard values (total µg CN^- per 50 mL standard volume) (x) versus the absorbance values (y) to determine correlation. If the correlation coefficient is less than 0.995, then the calibration curve should be rerun using new standards if necessary.

9.2.2 Using the regression analysis, calculate sample concentration (total µg CN^- per 50 mL developed solution) from the calibration curve.

9.2.3 Calculate µg/g CN^- in the sample using the following equation:

$$\mu g/g,\ CN^- = \frac{(total\ \mu g\ CN^-) \times 50\ mL}{sample\ wt.\ (g) \times receiving\ solution\ volume\ used\ for\ color\ development, mL} \qquad \text{D-52}$$

10. Documentation

10.1 Report sample results in mg/Kg on FORM I-HCIN. NOTE: µg/g is proportional to mg/Kg.

11. Glassware Cleaning for Cyanide Distillations

11.1 Cyanide quantitative determinations require the use of non-disposable glassware that must be cleaned prior to reuse. Since the levels of cyanide in individual samples may vary significantly, all glassware should be treated on a worst-case basis. The following protocol will be used:

11.1.1 Prior to removal from the hood, all glassware will be washed with soapy water followed by a water rinse. Any sample that remains on glassware at this stage should be removed with the use of organic solvents followed by a soapy water, water rinsing. It is important to remember that at this stage the glassware may be "visually clean" but still may present potential health hazards.

11.1.2 At this point the glassware should be transferred in the hood to a bath consisting of 75 mL/gallon microwash (or equivalent ammonia containing cleaner). The glassware can now be removed from the hood and the glassware either soaked in microwash for two hours or hand scrubbed using the microwash solution.

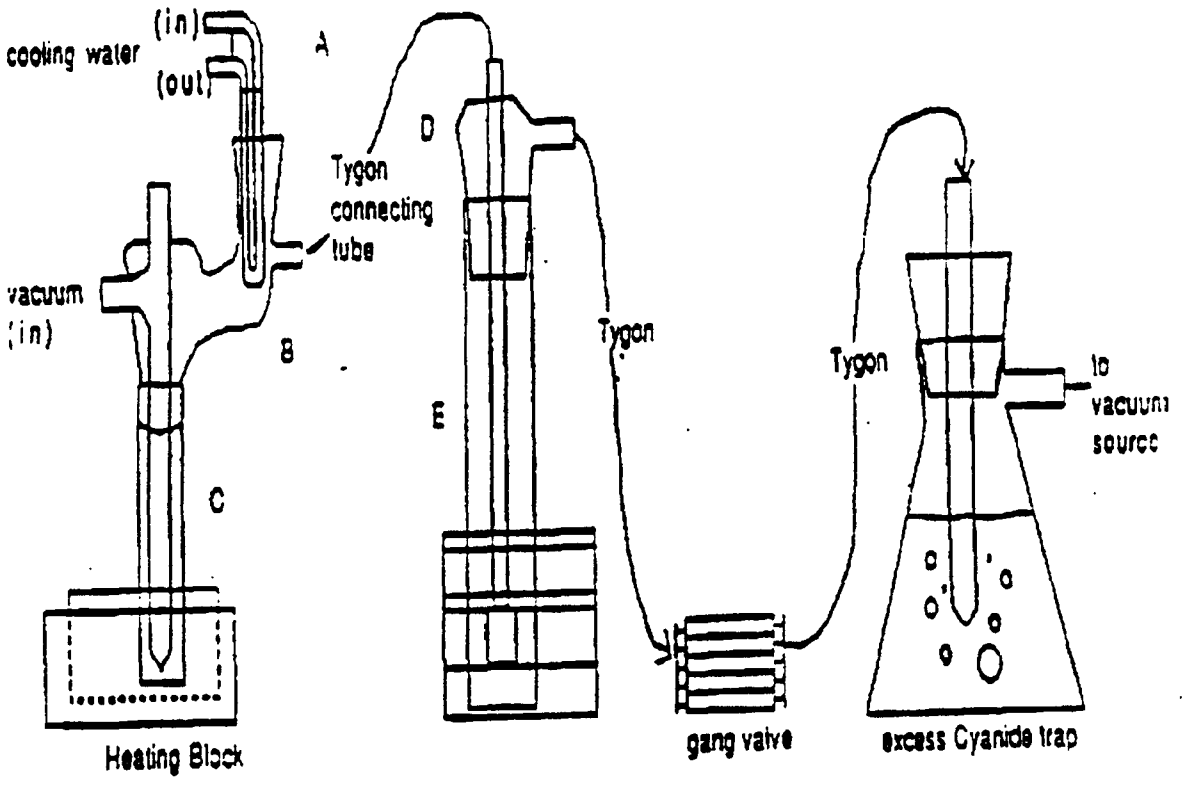
11.1.3 After appropriate rinsing to remove detergent, the glassware will be soaked in 25% HNO_3 for one hour or thoroughly rinsed with 50 percent HNO_3. Rinse all glassware with sufficient ASTM Type II water and then distilled water to remove all traces of acid.

11.1.4 Air dry the glassware or use an inert absorbent towel if the glassware is needed quickly.

11.1.5 Fritted glass impingers may be difficult to rinse. Rinsing may be aided by the use of compressed gas to blow out residual liquids.

Figure 1

CYANIDE DISTILLATION APPARATUS (MIDI)

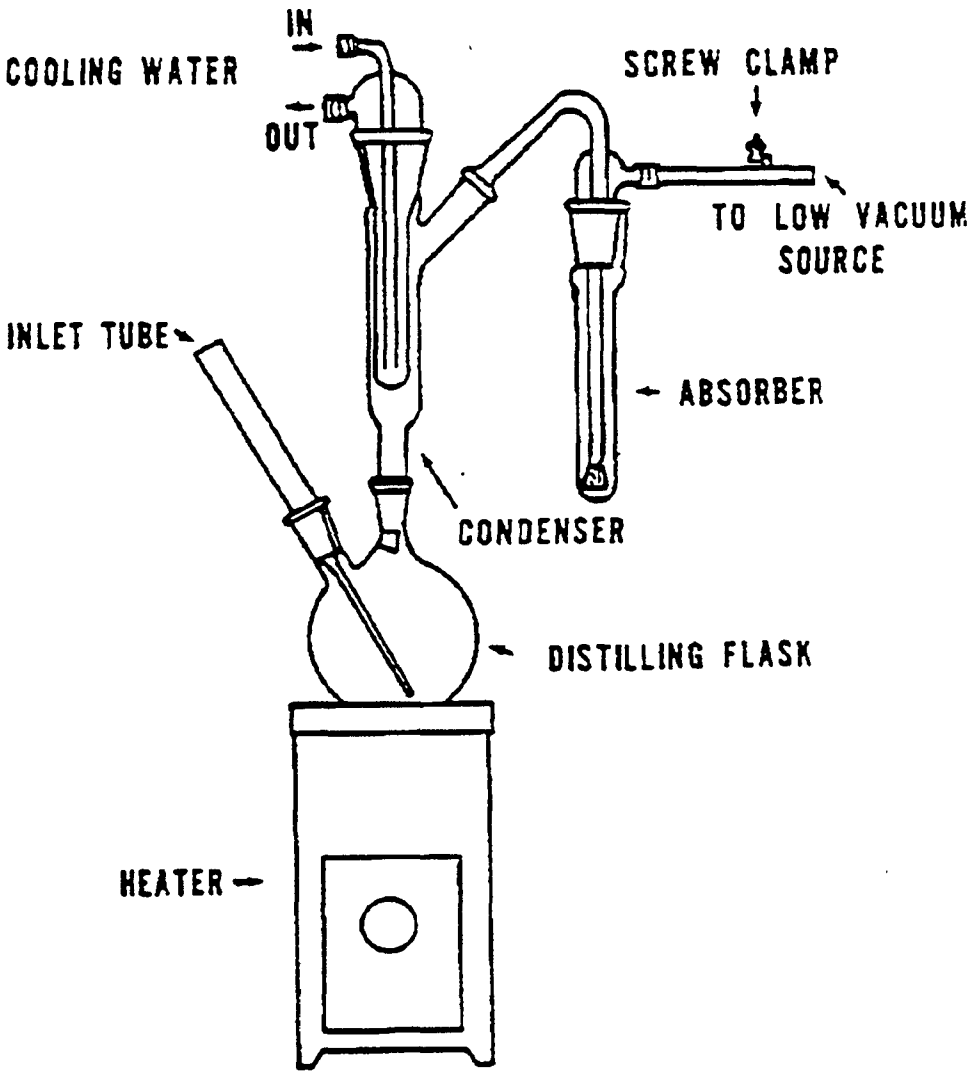


A = Microcondenser
B = Distillation Head
C = Impinger Tube (30ml)
(Reaction Vessel)

D = Fritted Glass Impinger
E = Impinger Tube (70 ml)
(Receiving Vessel)

Figure 2

CYANIDE DISTILLATION APPARATUS (ASTM Method D2036)



THIS PAGE LEFT INTENTIONALLY BLANK

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

EXHIBIT E

TABLE OF CONTENTS

Page

SECTION I - GENERAL QA/QC PRACTICES 221

SECTION II - SPECIFIC QA/QC PROCEDURES 223

SECTION III - LABORATORY EVALUATION PROCESS 243

SECTION I

GENERAL QA/QC PRACTICES

The Contractor shall adhere to standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus. The Contractor shall also adhere to laboratory practices with regard to reagents, solvents, and gases. 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, March 1979.

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein shall 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 shall also follow these procedures.

NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work shall be 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 in 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 handling, sample analysis, 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 the 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-LV. The Contractor can expect to analyze a preaward performance evaluation (PE) sample before contract startup and a quarterly PE sample with every SDG.

As specified in Exhibit B, the Contractor shall perform Quarterly Verification of Method Detection Limits (MDL) by the method specified in Exhibit D for the type and model of each instrument used on this contract, and shall submit results to SMO and EMSL-LV. All the MDLs shall meet the CRQLs specified in Exhibit C. For ICP methods, the Contractor shall also report, as specified in Exhibits B and D, linear range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this SOW, 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, not only do analytical samples include each of the phases of a field sample, including PE samples received from an external source, but also all required QA/QC samples (matrix spikes, analytical/post-digestion spikes, duplicates, LCS, ICS, CRQL standards, preparation blanks) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10 percent" means once every 10 analytical samples.

NOTE: Calibration blanks and calibration verification samples are not counted as analytical samples when determining 10 percent 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 must be repeated after taking the appropriate corrective action as specified in Exhibits D and E.

All QC measurements must be taken under the same conditions used to obtain sample measurements (i.e., if a continuing calibration verification is preceded or followed by a rinse, the sample analyzed must be preceded or followed by an equivalent rinse).

The Contractor must report all QC data in the exact format specified in Exhibit B.

1. **QA/QC Operations Described In This Exhibit**

1.1 Instrument Calibration.

1.2 Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV).

1.3 CRQL Standards for ICP and HYICP (CRI).

1.4 Linear Range Standard (LRS) Analyses.

1.5 Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses.

1.6 ICP Interference Check Sample (ICS) Analyses.

1.7 Spike Sample Analysis (S).

1.8 Analytical Spike Sample Analysis (AS).

1.9 Duplicate Sample Analysis (D).

1.10 Laboratory Control Sample (LCS) Analysis.

1.11 Method Detection Limit (MDL) Determination.

1.12 Interelement Corrections for ICP (ICP).

1.13 Hydride ICP (HYICP) QC Analysis.

2. **Quality Assurance Plan**

2.1 The Contractor shall establish a QA program with the objective of providing sound analytical chemical measurements. This program shall incorporate QC procedures, any necessary corrective action taken, all documentation required during data collection, and the quality assessment measures performed by management to ensure acceptable data production.

2.2 As evidence of such a program, the Contractor shall prepare a written Quality Assurance Plan (QAP) which describes the procedures that are implemented to achieve the following:

2.2.1 Maintain data integrity, validity, and useability;

2.2.2 Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility;

2.2.3 Detect problems through data assessment and establish corrective action procedures which keep the analytical process reliable; and

2.2.4 Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

2.2.5 The QAP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA/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 QAP are as follows:

- Organization and Personnel;
  - QA Policy and objectives;
  - QA Management;
    - a. Organization;
    - b. Assignment of QC/QA responsibilities;
    - c. QA document control procedures;
    - d. Reporting relationships; and
    - e. QA program assessment procedures.
  - Personnel;
    - a. Resumes;
    - b. Education and experience pertinent to this contract; and
    - c. Training progress.
- Facilities and equipment;
  - Instrumentation and backup alternatives; and
  - Maintenance activities and schedules.
- Document Control;

- Laboratory notebook policy;
- Samples tracking/custody procedures;
- Case file organization, preparation, and review procedures;
- Procedures for preparation, approval, review, revision, and distribution of SOPs; and
- Process for revision of technical or documentation procedures.

- Analytical methodology;
  - Calibration procedures and frequency;
  - Sample preparation/extraction procedures;
  - Sample analysis procedures;
  - Standards preparation procedures; and
  - Decision processes, procedures, and responsibility for initiation of corrective action.
- Data Generation;
  - Data collection procedures;
  - Data reduction procedures;
  - Data validation procedures; and
  - Data reporting and authorization procedures.
- Quality Assurance;
  - Data QA;
  - Systems/internal audits;
  - Performance/external audits;
  - Corrective action procedures;
  - QA reporting procedures; and
  - Responsibility designation.
- Data Validation/Self-Inspection Procedures;

- Data flow and chain-of-command for data review;
- Procedures for measuring precision and accuracy;
- Evaluation parameters for identifying systematic errors;
- Procedures to assure that hardcopy data are complete and compliant with the requirements in Exhibit B;
- Demonstration of internal QA inspection procedure (demonstrated by supervisory sign-off on personal notebooks, internal PE samples, etc.);
- Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas);
- Demonstration of problem identification, corrective actions taken, resumption of analytical processing resulting from an internal audit (i.e., QA feedback); and
- Documentation of audit reports (internal and external), response, corrective action, etc.

- Data Handling; and
  - Data Management; and

    a. Data management procedures are written procedures that are clearly defined for all databases and files used to generate or re-submit deliverables specifying the acquisition or entry, update, correction, deletion, storage, and security of computer readable data and files. Key areas of concern include: system organization including personnel and security, documentation, operations, traceability, and QC.

       (i) Data manually entered from hardcopy must be quality controlled and error rates estimated;

       (ii) System should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors;

       (iii) Data entry error rates must be estimated and recorded on a monthly basis by re-entering a statistical sample of the data entered and calculating discrepancy rates by data element;

       (iv) Record of changes in the form of corrections and updates to data originally generated, submitted, and/or re-submitted must be documented to allow traceability of updates. Documentation must include the following information 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 independent of the source generating the deliverable);
- Change documentation must be retained according to the schedule of the original deliverable;
- Resubmitted deliverables must be re-inspected as a part of the laboratory's internal inspection process prior to submission. The entire deliverable and not just the changes must be re-inspected;
- The laboratory manager must approve changes to originally submitted deliverables;
- Documentation of data changes may be requested by laboratory auditors;
- Life cycle management procedures must be applied to computer systems 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; and
- System and operations documentation must be developed and maintained for each system. Documentation must include a user's manual and an operations and maintenance manual.

■ Individual(s) responsible for the following documentation must be identified.

a. System operation and maintenance including documentation and training;

b. Database integrity including data entry, data updating and QC; and

c. Data and system security, backup, and archiving.

- Quality Control.

■ Solvent, reagent and adsorbent check analysis;

- Reference material analysis;
- Internal QC checks;
- Corrective action and determination of QC limit procedures; and
- Responsibility designation.

3. Instrument Calibration

3.1 Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments shall be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

3.2 The calibration standards must be prepared using the same type of matrix and at the same concentration as the preparation blank following sample preparation. The Contractor shall aspirate or inject the calibration solutions as described in the individual methods (see Exhibit D) and record the readings.

3.3 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 a CCV and a CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRQL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least one blank and one standard must be used for ICP and HYICP systems.

4. Initial Calibration Verification and Continuing Calibration Verification

4.1 Initial Calibration Verification

4.1.1 Immediately after each of the ICP, HYICP, GFAA, CVAA, 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 (ICV) solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 3-Initial and Continuing Calibration Verification (CCV) Control Limits for Inorganic Analyses (see Exhibit C), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

4.1.2 If the ICV 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.

4.1.3 For ICP, the ICV solution(s) must be run at each wavelength used for analysis. For cyanide, the initial calibration verification standard must be distilled with the batch of samples analyzed in association with that ICV because it serves as a Laboratory Control Sample (LCS). 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 calibration verification shall be recorded on FORM II-HCIN for ICP, HYICP, GFAA, CVAA, and cyanide analyses, as indicated.

4.2 Continuing Calibration Verification

4.2.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for CCV and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10 percent or every two hours during an analysis run, whichever is more frequent, and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near ± 10 percent of the mid-range levels of the calibration curve:

- EPA solutions; or
- A Contractor-prepared standard solution.

4.2.2 The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

4.2.3 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 apply 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 analyses 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.

4.2.4 If the deviation of the continuing calibration verification is greater than the control limits specified in Table 3 in Exhibit C, the analysis must be terminated, the problem corrected, and the CCV reanalyzed. If the reanalysis yields a CCV value within control limits, then the preceding 10 analytical samples or all analytical samples analyzed since the last acceptable calibration verification must be analyzed for the analytes affected. Otherwise, the instrument must be recalibrated, the calibration verified, and the affected analytical samples rerun. Each analytical sample must be bracketed by two consecutive CCVs that have been analyzed within two hours of each other with no more than 10 analytical samples run in between. In addition, the value for each analyte in those two CCVs must meet the control limits. Information regarding the continuing verification of calibration shall be recorded on FORM II-HCIN in Exhibit B for ICP, HYICP, GFAA, CVAA, and cyanide, as indicated.

5. CRQL Standards

5.1 To verify linearity near the CRQL for ICP, HYICP, GFAA, mercury, and cyanide analysis, the Contractor must analyze an CRQL standard at two times the CRQL or two times the MDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per eight hour working shift, whichever is more frequent, but not before ICV. This standard must be run for every wavelength used for analysis.

5.2 Results for the analysis of the CRQL standard must be within ± 25 percent of the true value for each wavelength used for analysis. If not, the analysis must be terminated, the problem corrected, and the analytical samples since the last acceptable CRQL standard reanalyzed.

5.3 The Contractor must analyze and report these standards on FORM III-HCIN in Exhibit B for each method.

6. Linear Range Standard Analysis

6.1 For ICP and HYICP analyses, a linear range check standard (LRS) must be analyzed within 30 days prior to and before the start of any contract analyses and at least quarterly (every three months). This standard must be run for every wavelength used for analysis.

6.2 Results for the analysis of the LRS must be within ± five percent of the true value for each wavelength used for analysis. If not, the analysis must be terminated and successive dilutions of the standard must be reanalyzed until the control limits are met. The concentration of this standard that meets the control limits is the upper limit of the instrument linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

6.3 The Contractor must analyze and report these standards on FORM III-HCIN in Exhibit B for each method.

7. Initial Calibration Blank, Continuing Calibration Blank, and Preparation Blank Analyses

7.1 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

7.1.1 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 percent or every two 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 and after the last analytical sample of the run.

7.1.2 The results for the calibration blanks shall be recorded on FORM IV-HCIN for ICP, HYICP, GFAA, CVAA, and cyanide analyses, as indicated. If the absolute value of the calibration blank result exceeds the method detection limit, the result must be reported in mg/L on FORM IV-HCIN. If the absolute value blank result exceeds the CRQL (Exhibit C), analysis must be terminated, the problem corrected, and the CCB reanalyzed. If the reanalysis yields a CCB with an absolute value below the CRQL, then all analytical samples analyzed since the last acceptable calibration blank must be reanalyzed. Otherwise, the instrument must be recalibrated, the calibration verified, and the affected analytical sample(s) rerun.

7.1.3 Each analytical sample must be bracketed by two consecutive CCBs that have been analyzed within two hours of each other with no more than 10 analytical samples run in between, and the absolute value for each analyte in these two CCBs must fall below the CRQL or MDL whichever is greater.

7.1.4 The flush time between any of the samples in a QC set cannot be less than the flush time between the last sample and the final CCB of that same set.

7.2 Preparation Blank (PB) Analysis

7.2.1 For each sample phase, at least one PB (or reagent blank), as described in the potassium hydroxide fusion procedure (Exhibit D, Section V, paragraph 2.4) must be prepared and analyzed with every SDG, or with each batch of samples digested, whichever is more frequent.

7.2.2 The first batch of samples in an SDG shall to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM IV-HCIN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

7.2.3 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:

- If the absolute value of the concentration of the blank is less than or equal to the Contract Required Quantitation Limit (Exhibit C), no correction of sample results is performed.

- If any analyte concentration in the blank is above the CRQL, all associated samples containing less than 10 times the blank concentration must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.

- If an analyte concentration in the blank is below the negative CRQL, all samples with a reported analyte value below 10 times CRQL and associated with the blank must be redigested and reanalyzed.

- The values for the preparation blank must be recorded in mg/Kg on FORM IV-HCIN for ICP, HYICP, GFAA, CVAA, and cyanide analyses.

8. ICP Interference Check Samples (ICS) Analysis

8.1 To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples (ICS) at the beginning and end of each analysis run or a minimum of twice per eight hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP ICS must be obtained from EPA EMSL-LV if available and analyzed according to the instructions supplied with the ICS.

8.2 The ICS consists of two solutions: Solution A and Solution AB. Solution A contains potential interferants, and Solution AB contains both analytes and interferants. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

8.3 Results for the ICP analyses of Solution AB during the analytical runs must be within ± 20 percent of the true value for the analytes included in the ICS. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last acceptable 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).

8.4 If the ICP ICS is not available from EPA, independent ICP Check Samples must be prepared with interferant and analyte concentrations at the levels specified in Table 2-Interferant and Analyte Elemental Concentrations used for ICP ICS (see Exhibit C). 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 V-HCIN. Results must be within ± 20 percent of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the ICS analyses must be recorded on FORM V-HCIN for all ICP parameters.

9. Spike Sample Analysis

9.1 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 sample preparation (i.e., prior to fusion, digestion or distillation). At least one spike sample analysis must be performed on each group of samples of similar phases for each SDG.[21]

9.2 The spike sample is prepared by adding 0.0125 g of the solid spiking mixture to a 0.25 g aliquot of sample which is then carried through the sample preparation procedure.

9.3 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 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.

9.4 If two analytical methods are used to obtain the reported values for the same metal within a SDG (i.e., ICP, HYICP), spike samples must be run by each method used.

9.5 If the spike recovery is not within the limits of 75-125 percent, the data for all of the samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-HCIN and VI-HCIN. 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 percent recovery criteria.

9.6 In the instance where there is more than one spike sample per phase 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.

9.7 Individual component percent recoveries (%R) are calculated as follows:

$$\%\ Recovery\ \frac{(SSR - SR)}{SA} \times 100 \qquad \text{E-1}$$

[21]EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

Where:
SSR = Spiked Sample Result;
SR = Sample Result; and
SA = Spike Added.

9.8 When the sample concentration is less than the method detection limit, use SR = 0 only for purposes of calculating percent recovery. The spike sample results, sample results and percent recovery (positive or negative) must be reported on FORM VI-HCIN for ICP, HYICP, GFAA, mercury, and cyanide analyses, as indicated.

10. Analytical Spike Sample Analysis

10.1 The analytical spike sample analysis is designed to provide information about the effect of the sample matrix on the measurement system. The spike is added after the sample has been prepared and prior to analysis. For ICP, HYICP, AA, and cyanide, at least one spike sample analysis must be performed on each group of samples of a similar phase for each SDG.[22]

10.2 If the analytical 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 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 spike sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

10.3 The analytical spike sample analysis must be performed on a sample containing measurable amounts of the analyte or at least a representative sample of the phases associated with it.

10.4 For the analytical spike sample analysis, each analyte must be spiked with a concentration equal to 30 percent of the analyte's linear range for HYICP and two times the CRQL for GFAA. The sample and spike sample must be at the same dilution.

10.5 If the spike recovery is not within the limits of 85-115 percent, a second analytical spike must be performed. If the second analytical spike is out of control then the preparation blank must be spiked with the same spiking solution. If spiking the blank yields a recovery that is out of control, the spiking solution must be reprepared and the previous spiking procedure repeated. If not, flag all samples received associated with that spike sample and determined by the same analytical method flagged with the letter "E" on FORMs I-HCIN and VII-HCIN (see Figure 3). The percent recovery is calculated in the same manner as that used for the matrix spike percent recovery calculation.

10.6 The spike sample results, sample results, spiking level and percent recovery (positive, negative or zero) must be reported on FORM VII-HCIN for ICP, HYICP, GFAA, mercury, and cyanide analysis.

[22]EPA may require additional spike sample analysis upon special request by the Project Officer, for which the Contractor will be paid.

11. Duplicate Sample Analysis

11.1 One duplicate sample must be analyzed from each group of samples of a similar phase for each SDG.[23] Duplicates cannot be averaged for reporting on FORM I-HCIN.

11.2 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., HYICP and GFAA), duplicate samples must be run by each method used.

11.3 The relative percent differences (RPD) for each component are calculated as follows:

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

Where:
RPD = Relative Percent Difference;
S = First Sample Value (original); and
D = Second Sample Value (duplicate)

11.4 The results of the duplicate sample analyses must be reported on FORM VIII-HCIN in mg/Kg. A control limit of ± 20 percent for RPD shall be used for original and duplicate sample values greater than or equal to five times CRQL (Exhibit C). A control limit of ± the CRQL must be used for sample values less than five times CRQL, and the absolute value of the control limit (CRQL) must be entered in the "CONTROL LIMIT" column on FORM VIII-HCIN.

11.5 If one result is above the five times CRQL level and the other is below, use the ± CRQL criteria. If both sample values are less than the MDL, the RPD is not reported on FORM VIII-HCIN.

11.6 If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk "*" on FORMs I-HCIN and VIII-HCIN. 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 phase 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 VIII-HCIN at a later date based on these precision results.

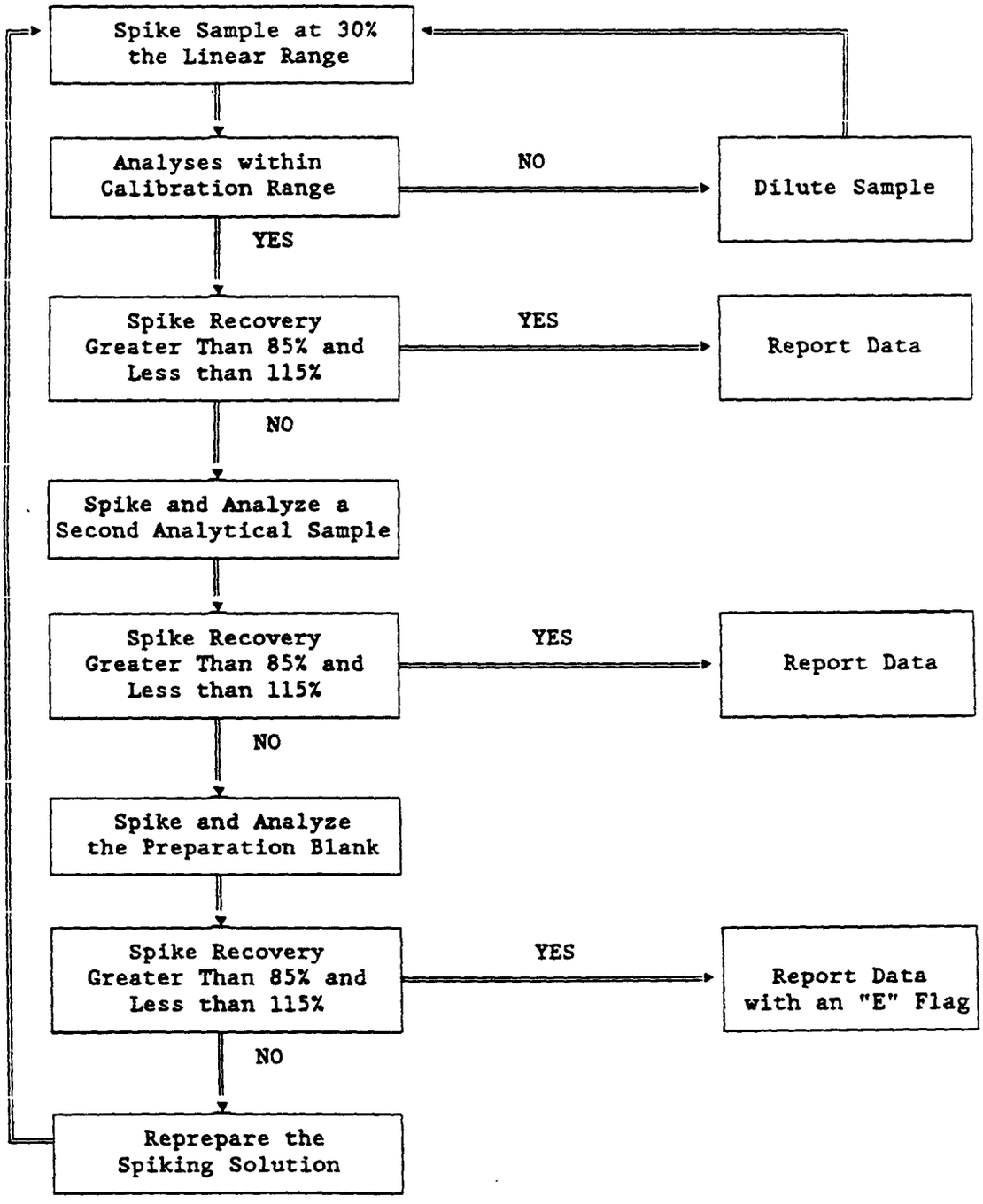
12. Laboratory Control Sample Analysis

12.1 The Laboratory Control Sample (LCS) must be analyzed for each analyte using the same sample preparation, analytical methods and QA/QC procedures employed for the EPA samples received.

---

[23]EPA may require additional duplicate sample analyses upon special request by the Project Officer, for which the Contractor will be paid.

FIGURE 3
Analytical Spike Analysis Scheme



12.2 The EPA-provided LCS must be prepared and analyzed using each of the procedures applied to the samples received. If the EPA LCS is unavailable, other EPA Quality Assurance check samples or other certified materials may be used. One LCS must be prepared and analyzed for every group of samples in a SDG, or for each batch of samples prepared, whichever is more frequent.

12.3 All LCS results, control limits and percent recovery (%R) shall be reported on FORM IX-HCIN.

12.4 If the results of the LCS are not within the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed.

13. Method Detection Limit (MDL) Determination

13.1 The Method Detection Limits (MDLs) (in mg/L) must be determined for each instrument used, within 30 days prior to and before the start of any contract analyses and at least quarterly (every three calendar months). The MDL must meet the CRQLs specified in Exhibit C.

13.2 The MDLs (in mg/L) are determined by multiplying by three the average of the standard deviations (σ_{n-1}) obtained on three nonconsecutive days from the consecutive analyses of seven different preparation blank dissolutions. 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). MDLs must be determined and reported for each wavelength used in the analysis of the samples.

13.3 The quarterly determined MDL for an instrument must always be used as the MDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the MDL, the MDL for that instrument must be redetermined and the results submitted for use as the established MDL for that instrument for the remainder of the quarter.

13.4 MDLs must be reported for each instrument on FORM XI-HCIN and submitted with each data package. If multiple instruments are used for the analysis of an analyte within a SDG, the highest MDL for the analyte must be used for reporting concentration values for that SDG.

13.5 The MDL for each analyte must be less than or equal to the CRQL. An exception is granted if the analyte concentration in the samples is greater than or equal to two times the reported method detection limit.

14. Interelement Corrections for ICP

14.1 The ICP interelement correction factors must be determined within three months prior to beginning sample analyses under this contract and at least annually thereafter. Correction factors for spectral interference must be determined at all wavelengths used for each analyte reported by ICP.

14.2 The correction factors must be determined under the same instrument conditions used for sample analysis. If the instrument was adjusted in any way that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. The interelement factors determination must be reported on FORM XIII-HCIN for all ICP analytes.

15. Hydride ICP (HYICP) and GFAA QC Analyses

15.1 Because of the nature of the GFAA and HYICP techniques, the special procedures summarized in Figures 4 and 5 will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

15.1.1 All analyses must fall within the calibration range. In addition, all analyses, except during full Methods of Standard Addition (MSA), will require duplicate exposures/injection to be reported in raw data as well as the average intensity and concentration values. A maximum of 10 full sample analyses to a maximum of 20 exposures/injections may be performed between each consecutive calibration verification and blank. The raw data package must contain intensity and concentration values for both exposures/injections, the average value and the relative standard deviation (RSD) or coefficient of variation (CV). For concentrations greater than CRQL, the duplicate exposure/injection readings must agree within 20 percent RSD or CV, or the analytical sample must be rerun once (i.e., two additional exposures/injections). If the readings are still out, flag the value reported on FORM I-HCIN 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-HCIN for that sample.

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, respike and reanalyze all analytical samples associated with that blank.

15.1.2 All HYICP and GFAA 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 will be required to be at a concentration (in the sample) of 30 percent of the linear range (in mg/L) for HYICP and two times the CRQL for GFAA. 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. MSAs are 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 the control limits (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 respike and reanalyze all analytical samples associated with the blank. An analytical spike is not required on the pre-digestion spike sample.

15.1.3 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 Spike Sample Analysis, this exhibit), will then determine how the sample will be quantitated, as follows:

- If the spike recovery is less than 40 percent, the sample must be diluted by a factor of five and rerun with another spike. This step must only be performed once. If after the dilution the spike recovery is still less than 40 perecent, report data from the initial undiluted analysis and flag with an "E" to indicate interference problems.

- If the spike recovery is at or between 85 perecent and 115 perecent, the sample must be quantitated directly from the calibration curve and reported down to the MDL.

- If the spike recovery is greater than 40 perecent and less than 85 perecent or greater than 115 perecent, the sample must be quantitated by MSA.

- The following procedures will be incorporated into MSA analyses:

  - Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

  - The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial' spike run data are 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 perecent QC frequency (i.e., five full MSAs can be performed between calibration verifications).

  - For analytical runs containing only MSAs, single exposures/injections can be used for QC samples during that run.

  - HYICP Spikes must be prepared such that:

    a. Spike 1 is approximately 20 perecent of the linear range in mg/L.

    b. Spike 2 is approximately 40 perecent of the linear range in mg/L.

    c. Spike 3 is approximately 60 perecent of the linear range in mg/L.

  - The data for each MSA analysis must be clearly identified in the raw data documentation (spike concentrations measured intensities or concentration, x-intercept, y-intercept and correlation coefficient). The results shall be reported on FORM X-HCIN. Reported values obtained by MSA must be flagged on FORM I-HCIN with the letter "S" if the correlation coefficient is greater than or equal to 0.995.

  - 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 X-HCIN, report the results of both MSA analysis and flag with a "+" for any MSA result that yields a correlation coefficient less than 0.995.

  - GFAA Spikes must be prepared such that:

    a. Spike 1 is approximately 50 perecent of the sample concentration in mg/L.

    b. Spike 2 is approximately 100 perecent of the sample concentration in mg/L.

    c. Spike 3 is approximately 150 perecent of the sample concentration in mg/L.

  - The data for each MSA analysis must be clearly identified in the raw data documentation (spike concentrations measured intensities or concentration, x-intercept, y-intercept and correlation coefficient). The results shall be reported on FORM X-HCIN. Reported values obtained by MSA must be flagged on FORM I-HCIN with the letter "S" if the correlation coefficient is greater than or equal to 0.995.

FIGURE 4

GFAA Spike Analysis Scheme

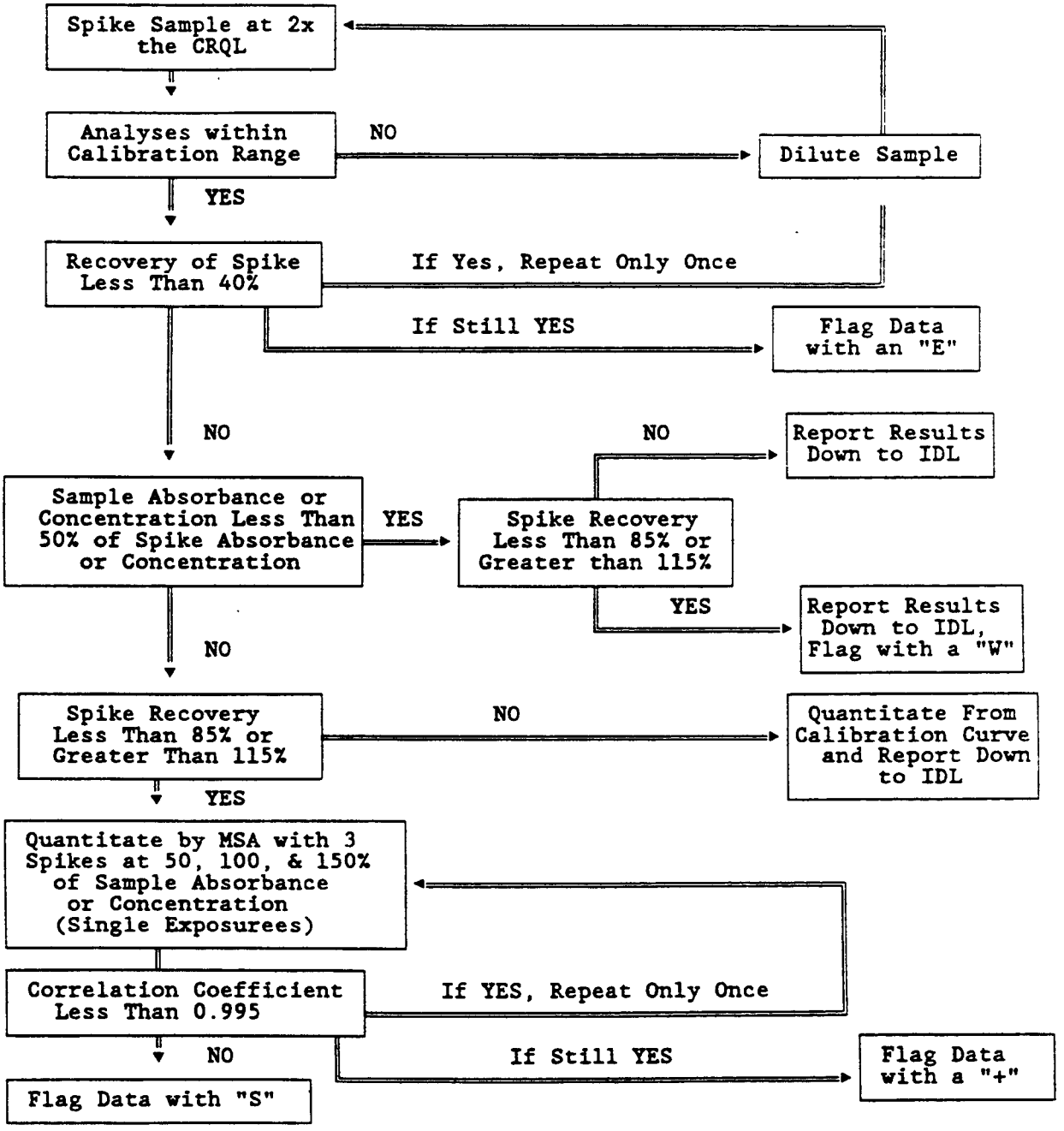
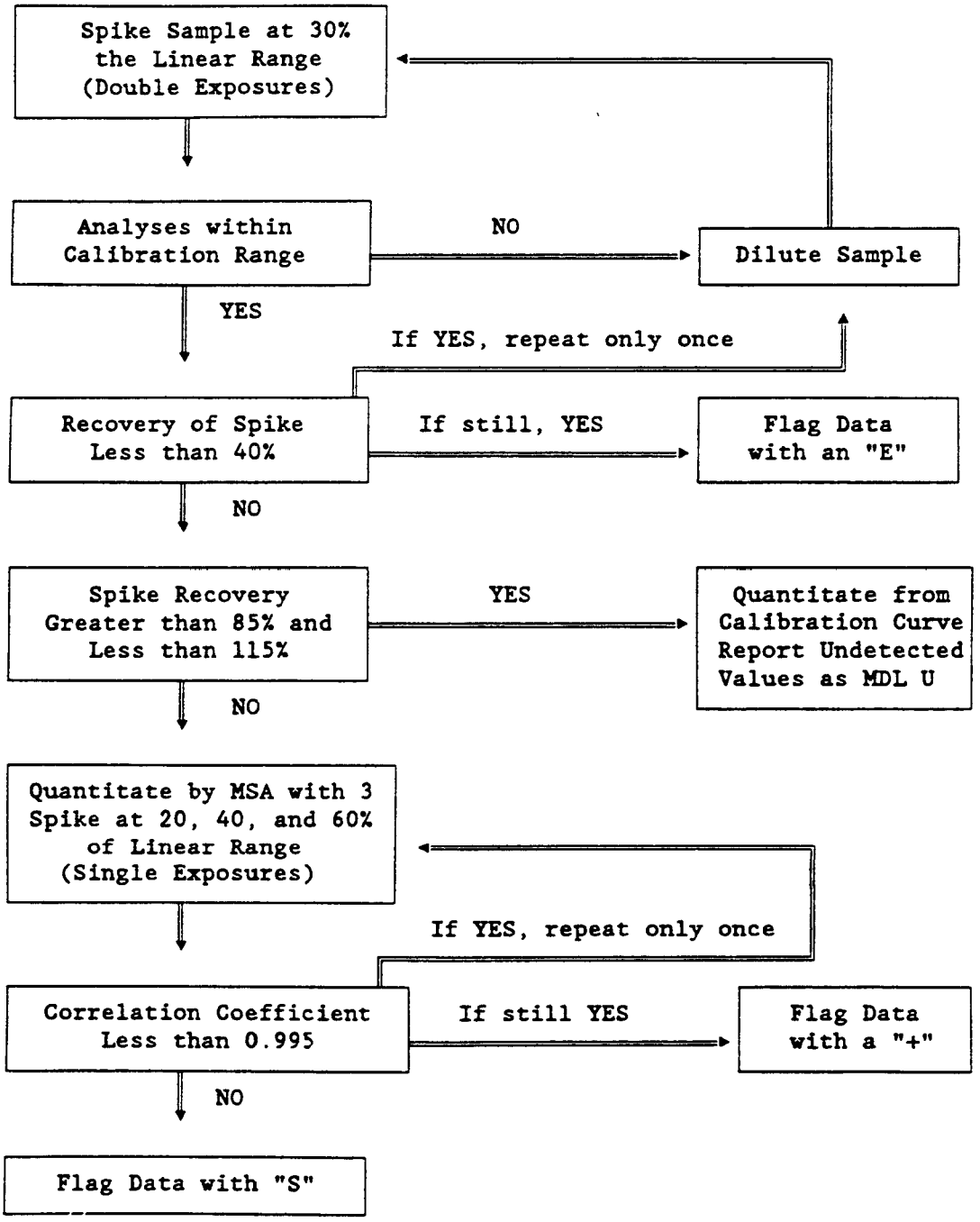


FIGURE 5

Hydride ICP Absorption Analyses Scheme



- 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 X-HCIN, report the results of both MSA analysis and flag with a "+" for any MSA result that yields a correlation coefficient less than 0.995.

SECTION III

LABORATORY EVALUATION PROCESS

This document outlines the procedures which will be used by the EPA Administrative or Technical Project Officer or his/her authorized representative to conduct laboratory audits to determine the Contractor's ability to meet the terms and conditions of this contract. The evaluation process incorporates two major steps:

- Evaluation of laboratory performance; and
- On-site inspection of the laboratory to verify continuity of personnel, instrumentation and quality control requirements of the contract.

1. Evaluation of Laboratory Performance

1.1 Preaward Performance Evaluation Sample Analysis

1.1.1 The Preaward Performance Evaluation sample set will be sent to a participating laboratory before the contract award, to verify the laboratory's ability to produce acceptable analytical results.

1.1.2 When the preaward data are received by EPA, results will be scored for identification and quantitation. The Contractor will be notified of acceptability/nonacceptability within 45 days.

1.2 Performance Evaluation Sample Analysis

1.2.1 The Performance Evaluation sample will assist the EPA in monitoring contractor performance. The laboratory will not be informed of the analytes in the PE sample or their concentration.

1.2.2 The Performance Evaluation sample set will be sent to a participating laboratory on a quarterly basis to verify the laboratory's continuing ablility to produce acceptable analytical results. These samples will be provided either single blind (recognizable as a PE material and of unknown composition), or double blind (not recognizable as PE material and of unknown composition). If received as a single blind, the Contractor is required to submit PE sample data in a separate SDG package in accordance with Delivery Schedule requirements for PE Sample data. PE samples received as double blind would be treated as routine samples and data would be submitted in the SDG deliverables package per normal procedure.

1.2.3 The Contractor shall prepare and analyze the PE samples using the procedure described in the sample preparation and method analysis sections of Exhibit D of this Statement of Work. All contract-required QC shall also be met.

1.2.4 In addition to PE samples preparation and analysis, the Contractor shall be responsible for correctly identifying and quantifying the analytes included in the PE sample. The EPA will notify the Contractor of unacceptable performance.

NOTE: Unacceptable performance for identification and quantification of analytes in the PES is defined as a score less than 50 percent.

1.2.5 When the PE data are received by EPA, results will be scored routinely for identification and quantitation. Results of these scoring will be provided for the Contractor via coded evaluation

spreadsheets by analyte. The Government may adjust the score on any given PE sample to compensate for unanticipated difficulties with a particular sample.

1.2.6 The Contractor shall demonstrate acceptable performance for analyte identification and quantification. If the Contractor achieves a score of less than 50 percent, the EPA may take, but is not limited to, the following actions:

- Show Cause and/or Cure Notice;
- Reduction of the number of samples shipped to the laboratory;
- Suspension of sample shipment;
- A site visit;
- A full data audit; and/or
- Require the laboratory to analyze a remedial PE sample.

1.3 Inorganic Data Audit

1.3.1 Inorganic data audits are conducted by EMSL-LV on the Contractor's sample data packages. The inorganic data audit provides the Agency with an in-depth inspection and evaluation of the data packages with regard to achieving QA/QC acceptability.

2. On-Site Laboratory Evaluation

2.1 The on-site laboratory evaluation helps to ensure that technical competence is maintained and that all the necessary quality control is being applied by the Contractor in order to deliver a quality product.

2.2 On-site laboratory evaluations allow the evaluators to determine that:

- The organization and personnel are qualified to perform assigned tasks;
- Adequate facilities and equipment are available;
- Complete documentation, including chain-of-custody of samples, is being implemented;
- Proper analytical methodology is being used;
- Adequate analytical quality control, including reference samples, control charts, and documented corrective action measures, is being provided; and
- Acceptable data handling and documentation techniques are being used.

2.3 The on-site visit also serves as a mechanism for discussing weaknesses identified through PE sample analysis or through Contract Compliance Screening or review of other data deliverables.

2.4 The on-site visit allows the evaluation team to determine if the laboratory has implemented the recommended and/or required corrective actions, with respect to quality assurance, that were made during the previous on-site visit.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND STANDARD OPERATING PROCEDURES

EXHIBIT F

TABLE OF CONTENTS

Page

SECTION I: CHAIN-OF-CUSTODY 247

SECTION II: DOCUMENT CONTROL 249

SECTION III: STANDARD OPERATING PROCEDURES 253

SECTION I

CHAIN-OF-CUSTODY

A sample is physical evidence collected from a facility or from the environment. An essential part of a hazardous waste investigation effort is that the evidence gathered be controlled. To accomplish this, the following sample identification, chain-of-custody, sample receiving, and sample tracking procedures have been established.

1. Sample Identification

1.1 To ensure traceability of samples while in possession of the Contractor, the Contractor shall have a specified method for maintaining identification of samples throughout the laboratory.

1.2 Each sample or 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.

2. Chain-of-Custody Procedures

2.1 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 to authorized personnel only.

3. Sample Receiving Procedures

3.1 The Contractor shall designate a sample custodian responsible for receiving all samples.

3.2 The Contractor shall designate a representative to receive samples in the event that the sample custodian is not available.

3.3 The condition of the shipping containers and sample bottles shall be inspected upon receipt by the sample custodian or his/her representative.

3.4 The condition of the custody seals (intact/not intact) shall be inspected upon receipt by the sample custodian or his/her representative.

3.5 The sample custodian or his/her representative shall check for the presence or absence of the following documents accompanying the sample shipment:

- Airbills or airbill stickers;

- Custody seals;
- EPA custody records;
- EPA Traffic Reports or SAS packing lists; and
- Sample tags.

3.6 The sample custodian or his/her representative shall sign and date all forms (i.e., custody records, Traffic Reports or packing lists, and airbills) accompanying the samples at the time of sample receipt.

3.7 The Contractor shall contact SMO to resolve discrepancies and problems such as absent documents, conflicting information, broken custody seals, and unsatisfactory sample condition (e.g., leaking sample bottle).

3.8 The Contractor shall record the resolution of discrepancies and problems on Telephone Contact Logs.

3.9 The following information shall be recorded on FORM HDC-1 by the sample custodian or his/her representative as samples are received and inspected:

- Condition of the shipping container;
- Presence or absence and condition of custody seals on shipping and/or sample containers;
- Custody seal numbers, when present;
- Condition of the sample bottles;
- Presence or absence of airbills or airbills stickers;
- Airbill or airbill sticker numbers;
- Presence or absence of EPA custody records;
- Presence or absence of EPA Traffic Reports or SAS packing lists;
- Presence or absence of sample tags;
- Sample tag identification numbers cross-referenced to the EPA sample numbers;
- Verification of agreement or non-agreement of information recorded on shipping documents and sample containers; and
- Problems or discrepancies.

4. Sample Tracking Procedures

4.1 The Contractor shall maintain records documenting all phases of sample handling from receipt to final analysis. The records shall include documentation of the movement of samples and prepared samples into and out of designated laboratory storage areas.

SECTION II

DOCUMENT CONTROL

The goal of the laboratory document control program is to assure that all documents for a specified 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, document control form, 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 the EPA or are available upon request from the EPA prior to the delivery schedule.

1. Preprinted Data Sheets and Logbooks

1.1 All documents produced by the Contractor that 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 complied, all original laboratory forms and copies of all SDG related logbook entries shall be included in the documentation package.

1.2 The Contractor shall identify the activity recorded on all laboratory documents that is directly related to the preparation and analysis of EPA samples.

1.3 Pre-printed laboratory forms shall contain the name of the laboratory and shall be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

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.

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.

1.6 Pages in both bound and unbound logbooks shall be sequentially numbered.

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 the 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.

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 un readable. All notations shall be recorded in ink. Unused portions shall be "z'd" out (i.e., draw a large Z on the unused portion of the page).

2. Consistency of Documentation

2.1 The Contractor shall assign a document control officer (DCO) responsible for the organization and assemblance of the CSF.

2.2 All copies of laboratory documents shall be complete and legible.

2.3 Before releasing analytical results, the DCO shall assemble and cross-check the information on sample tags, custody records, lab bench sheets, personal and instrument logs, and other relevant data to ensure that data pertaining to each particular sample or sample delivery group is consistent throughout the CSF.

3. Document Numbering and Inventory Procedure

3.1 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, Section II.

3.2 All documents relevant to each SDG, including logbook pages, bench sheets, screening records, re-preparation records, re-analysis records, records of failed or attempted analysis, custody records, etc., shall be inventoried.

3.3 The DCO shall be responsible for ensuring that all documents generated are placed in the CSF for inventory and are delivered to EPA. The DCO shall place the sample tags in plastic bags in the file. Figure 5 is an example of a document inventory.

4. Storage of EPA Files

4.1 The Contractor shall maintain EPA laboratory documents in a secure location. Access shall be limited to only designated personnel.

5. Shipping Data Packages and Complete Sample Delivery Group File (CSF)

5.1 The Contractor shall document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that the containers 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.

5.2 The Contractor shall purge the CSF deliverable to the appropriate EPA Region 180 days after the report submission.

5.3 A copy of the transmittal letter for the CSF will be sent to NEIC and SMO.

5.4 **Sample Log-In Sheet**

5.4.1 This form is used to document the receipt and inspection of shipping containers and samples. The Contractor shall submit one (1) original FORM HDC-1 for each shipping container.

5.4.2 The Contractor shall sign and date the airbill (if present), examine the shipping containers, record the presences or absence of custody seals and their conditions.

5.4.3 The Contractor shall note any problems with the samples and follow the instructions explained in Exhibit B, Sample Log-In Sheet.

5.4.4 The Contractor shall submit a completed Sample Log-In Sheet with each SDG package.

Figure 5

Example

232-2-0001
Case No. ____
Region ____

DOCUMENT INVENTORY

Document Control #[24]	Document Type	# Pages
232-2-0001	Case File Document Inventory Sheet	1
232-2-0002	Chain-of-Custody Records	2
232-2-0003	Shipping Manifests	2
232-2-0004	Sample Tags	50
232-2-0005	SMO Inorganics Traffic Reports	10
232-2-0006	Inorganics Analysis Data Summary Sheets	10
232-2-0007	Analysts' Notebook Pages	14
232-2-0008	ICP and AA Instrument Logbook Pages	12

[24]This number is to recorded on each set of documents.

THIS PAGE LEFT INTENTIONALLY BLANK

SECTION III

STANDARD OPERATING PROCEDURES

The Contractor shall have written standard operating procedures (SOPs) for the following:

- Sample receipt and logging;
- Sample and extract storage;
- Preventing sample contamination;
- Security for laboratory and samples;
- Traceability/equivalency of standards;
- Maintaining instrument records and bound logbooks;
- Glassware cleaning;
- Technical and managerial review of laboratory operation and data package preparation;
- Internal review of contractually-required QA/QC data for each individual data package;
- Sample analysis, data handling, and data reporting;
- Chain-of-custody; and
- Document control, including Complete SDG File preparation.

1. Specifications for Written Standard Operating Procedures

1.1 An SOP is defined as a written narrative stepwise description of laboratory operating procedures including examples of laboratory documentation. The SOPs should describe accurately 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 the EPA as the basis for laboratory evidence audits.

1.2 The Contractor shall have written SOPs describing the sample custodian's duties and responsibilities.

1.3 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:

- Presence or absence of EPA chain-of-custody forms;

- Presence or absence of airbills or airbill stickers;
- Presence or absence of Traffic Reports or SAS packing lists;
- Presence or absence of custody seals on shipping and/or sample containers and their condition;
- Custody seal numbers, when present;
- Airbill or airbill sticker numbers;
- Presence or absence of sample tags;
- Sample tag ID numbers;
- Condition of the shipping container;
- Condition of the sample bottles;
- Verification of agreement or nonagreement of information on receiving documents and sample containers;
- Resolution of problems or discrepancies with the Sample Management Office; and
- The definition of any terms used to describe sample condition upon receipt.

1.4 The Contractor shall have written SOPs for maintaining identification of EPA samples throughout the laboratory.

1.5 If the Contractor assigns unique laboratory identifiers, written SOPs shall include a description of the method used to assign the unique laboratory identifier and cross-reference to the EPA sample number.

1.6 If the Contractor uses prefixes or suffixes in addition to sample identification numbers, the written SOPs shall include their definitions.

1.7 The Contractor shall have written SOPs for organization and assembly of all documents relating to each EPA Case, including technical and managerial review. Documents shall be filed on a Case-specific basis. The procedures must ensure that all documents including logbook pages, sample tracking records, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the Case are compiled in one location for submission to EPA. The system must include a document numbering and inventory procedure.

1.8 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.

1.9 The Contractor shall have written SOPs describing the method by which the laboratory maintains samples under custody.

2. Handling of Confidential Information

2.1 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.

2.2 All confidential documents shall be under the supervision of a designated Document Control Officer (DCO).

2.3 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 logs these documents into a Confidential Inventory Log. The information is then made 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 Contracting Officer. The DCO will enter all copies into the document control system. In addition, this information may not be disposed of except upon approval by the EPA Contracting Officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record of the disposition in the Confidential Inventory Log.

THIS PAGE LEFT INTENTIONALLY BLANK

EXHIBIT G

GLOSSARY OF TERMS

THIS PAGE LEFT INTENTIONALLY BLANK

Glossary of Terms

ALIQUOT - A measured portion of a field sample taken for analysis.

ANALYSIS DATE/TIME - The date and military time (24-hour clock) of the injection of the sample, standard, or blank into the analysis system.

ANALYSIS GROUP - An analysis group is a set of no more than 20 analytical samples (as defined below) for the purpose of method Quality Assurance/Quality Control (QA/QC), such that the QA/QC required by Exhibit E is, at a minimum, prepared and analyzed at a frequency of once per 20 analytical samples.

ANALYSIS REPLICATE - A single analytical sample processed through the analytical preparation method and analyzed in replicate.

ANALYSIS RUN - The actual instrumental analysis of the sample preparations from the time of instrument calibration through the running of the final continuing calibration verification (CCV). All sample preparation analyses during the analysis run are subject to the QC protocols set forth in Exhibit E of this contract unless otherwise specified in the individual methods.

ANALYSIS SPIKE SAMPLE - An analytical sample taken through the analytical preparation method and then spiked prior to analysis.

ANALYTE - The element or ion an analysis seeks to determine; the element of interest.

ANALYTICAL PREPARATION - An analytical sample taken through the analytical preparation method. Also referred to as preparation or sample preparation.

ANALYTICAL PREPARATION METHOD - A method (digestion, dilution, extraction, fusion, etc.) used to dissolve or otherwise release the analyte(s) of interest from its matrix and provide a final solution containing the analyte which is suitable for instrumental or other analysis methods.

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, CRQL standard for ICP (CRI) and AA (CRA), laboratory control sample, preparation blank, and linear range analysis sample.

ANALYTICAL SPIKE - A post-digestion spike to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the prepared sample. The unspiked sample aliquot must compensate for any volume change in the spike samples by addition of ASTM Type II water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10 percent of the analytical sample volume.

ASTM TYPE II WATER - Distilled water with a conductivity of less than 1.0 μmho/cm at 25°C. For additional specifications refer to ASTM D1193-77, "Standard Specification for Reagent Water."

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.

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 reagents and concentration of acids as used in the sample preparation.

CALIBRATION BLANK - A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation. This blank is not subjected to the preparation method but is produced synthetically.

CONTINUING CALIBRATION VERIFICATION (CCV) - A single element or multi-element standard solution prepared by the analyst to be used to verify the stability of the instrument calibration with time and the instrument performance during the analysis of samples. The CCV can either be one or more of the calibration standards and/or an initial calibration verification (ICV). However, all analyte elements being measured by the particular system must be represented in this standard, and the standard must have the same matrix as the samples. The CCV should have a concentration in the middle of the calibrated range. Analytical standard run every 10 analytical samples or every two hours, whichever is more frequent, to verify the calibration of the analytical system.

CALIBRATION STANDARDS - A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions are not subjected to the preparation method but contain the same matrix as the sample preparations to be analyzed.

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.

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) - 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.

DDI - Deionized distilled water.

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.

EBCDIC - Extended Binary Coded Decimal Interchange Code.

EXPOSURE - A full measurement of an emission line of an analyte from which the concentration of the analyte can be determined in the excitation system in a manner that meets the system's detection limit. It is also referred to as a peak scan.

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.

GEL - A two-phase colloidal system consisting of a solid and a liquid which behave as elastic solids and retain their characteristic shape.

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 (digestion or distillation).

Holding time = (sample analysis date - sample receipt date)

HYICP - Hydride Inductively Coupled Plasma.

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.

INITIAL CALIBRATION VERIFICATION (ICV) - Solution(s) obtained from the EPA or prepared from stock standard solutions, metals or salts obtained from a source separate from that (those) utilized to prepare the calibration standards and that have known concentration values. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV is not restricted to preparations made by official agencies when EPA sources are not available but should be traceable to the National Institute of Standards and Technology (NIST) or other certified standard.

INTERFERENCE CHECK SAMPLE (ICS) - Solution(s) containing both interfering and analyte elements of known concentrations that can be used to verify background and interelement correction factors. This solution must also contain the same matrix as the analytical preparations.

INTERFERANTS - Substances which affect the analysis for the element of interest.

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 - The concentration range over which the analytical curve remains linear. The range of the instrument for a specific analyte, as determined using calibration standards. The upper limit of this linear range (determined at each analysis) is the highest concentration calibration standard that has a determined value within 10 percent of the known value.

MATRIX - The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

MATRIX MODIFIER - Salts used in AA to lessen the effects of chemical interferants, viscosity, and surface tension.

MATRIX SPIKE - Aliquot of a sample 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 BLANK - A solution produced by performing the analytical preparation method without the addition of a sample. The solution thus contains the same concentrations of reagents as all other analytical preparations plus any impurities derived from the preparation process. For preparations containing reagents of variable concentrations, the method blank should match the maximum reagent concentration used in the sample preparation(s).

METHOD DETECTION LIMIT (MDL) - The chemical concentration that produces a signal, due to an analyte, which is equal to the student $t_{.99}$ times the standard deviation of a series of measurements on at least seven separate method blanks. In practice, a method detection limit will be substantially higher than an instrumental detection limit. The method detection limit for metals is $t_{.99}$ times the standard deviation of seven method blank analyses. All spectral background techniques must be operative and the same integration times must be utilized as when actual samples are analyzed.

METHOD OF STANDARD ADDITIONS (MSA) - The addition of three 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 percent of the volume). Standard addition may counteract matrix effects; it will not counteract spectral effects. Also referred to as Standard Addition.

MISCIBILITY - The ability of a liquid to dissolve uniformly in another liquid. If equal portions of two liquids are mixed and no interfacial meniscus is observed, the liquids are miscible. If a meniscus is observed without an apparent change in volume of the two liquids, the liquids are non-miscible. If there is an obvious change in the volume of the liquids, and a meniscus is observed, the liquids are partially miscible.

PERFORMANCE EVALUATION SAMPLE (PES) - A sample of known composition provided by EPA for Contractor analysis. Used by EPA to evaluate Contractor performance.

PHASE - The physical state of the sample or analytical sample which may be described as: water miscible (w), non-water miscible (n) or solid (c) (see Method 50.60-CLP).

PREPARATION LOG - An official record of the sample preparation (digestion).

PRIORITY POLLUTANT - Any substance introduced into the environment that the EPA classifies as being an immediate danger to the health and welfare of human life.

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 SET - A group of 10 analytical samples plus the CCVs and CCBs that bracket those samples.

ROUNDING RULES (EPA) - If the figure following those to be retained is less than five, 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 five, the figure is dropped, and the last retained figure is raised by one. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is five, and if there are no figures other than zeros beyond the five, the figure five 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.

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.

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.

SERIAL DILUTION - The dilution of a sample by a known factor. 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 interferants.

STOCK SOLUTION - A standard solution which can be diluted to derive other standards.

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.

VIEWING AREA ADJUSTMENT STANDARD - A solution containing a standard of a strong atom line (i.e., Cu) and a weak ion line (i.e., Ba) used to verify the proper adjustment of the observation height in the plasma for metals analysis by ICP (see Method 200.62-B-CLP for details).

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.