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SUPERFUND ANALYTICAL METHODS FOR LOW CONCENTRATION WATER FOR INORGANICS ANALYSIS

REPRODUCED BY
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SUPERFUND ANALYTICAL METHODS

FOR

LOW CONCENTRATION WATER FOR INORGANICS ANALYSIS

10/91

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

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

R5 025 3672

SECTION I - CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

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

Item	No. Copies	Delivery Schedule	Distribution (1)	(2)	(3)	(4)
*****A. Standard Operating Procedures	3	60 days after contract award, and as required in Exhibit E		X	X	X
B. Sample Traffic Reports	1	3 days after receipt of last sample in Sample Delivery Group (SDG)***	X			
**C. Sample Data Package	2	14 days after receipt of last sample in SDG	X		X	
D. Data in Computer Readable Format	1	14 days after receipt of last sample in SDG	X			
****E. Complete SDG File	1	14 days after receipt of last sample in SDG**		X		
*F. Quarterly/Annual Verification of Instrument Parameters	2	Quarterly: 15th day of January, April July, October	X		X	
*G. ICP/MS Diskettes/Tapes	Lot	Retain for 365 days after submission; or submit them within 7 days of written request by SMO or EMSL/LV	As directed			
*****H. Quality Assurance Plan	3	60 days after contract award, and as required in Exhibit E	As directed			

Distribution:
(1) Sample Management Office (SMO)
(2) Region-Client
(3) Environmental Monitoring Systems Laboratory (EMSL)
(4) National Enforcement Investigations Center (NEIC)

* Also required in each Sample Data Package.

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

*** Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 7 days or less and not exceeding 20 samples. Data for all samples in the SDG are due concurrently..

**** Complete SDG File will contain the sample data package plus all of the original documents described in Exhibit B under "Complete SDG File." The Complete SDG File must be delivered concurrently with the Sample Data Package.

*****See Exhibit E for a more detailed description.

NOTE: As specified in the Contract Schedule, unless otherwise instructed by SMO, the Contractor shall dispose of unused sample volume and used sample bottles/containers no earlier than sixty (60) days following submission of analytical data. Sample disposal and disposal of unused sample bottles/containers is the responsibility of the Contractor and should be done in accordance with all applicable laws and regulations governing the disposal of such material.

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, 2nd Floor
Alexandria, VA 22314

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

(3) USEPA Environmental Monitoring Systems Laboratory (EMSL)
944 E. Harmon Avenue
Las Vegas, NV 89109

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

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

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

All reports and documentation shall be:

- Legible,
- Clearly labeled and completed in accordance with instructions in this Exhibit,
- Arranged in the order specified in this Section,
- Paginated in ascending order, and
- Single-sided.

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

Whenever the Contractor is required to submit or resubmit data as a result of an on-site laboratory evaluation, a CCS assessment, or through a SMO action or a Regional data reviewer's request, the data shall be clearly marked as Additional Data and shall be sent to all three contractual data recipients (SMO, EMSL/LV, and the Client Region). A cover letter shall be included which describes which data are being delivered, to which Case(s) the data pertain, and who requested the data.

Whenever the Contractor is required or requested to respond to Contract Compliance Screening (CCS) review by SMO, the laboratory response shall be sent to all three contractual data recipients (SMO, EMSL/LV, and Region). In all three instances the response shall be accompanied by a color-coded Cover Sheet (Laboratory Response To Results of Contract Compliance Screening) which shall be provided in generic format by SMO.

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

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

A. Standard Operating Procedures (SOPs) and Quality Assurance Plan (QAP)

Submit updated SOPs and QAP according to the instructions in Exhibit E.

B. Sample Traffic Reports

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

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

The SDG Cover Sheet shall contain the following items:

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

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

Each Traffic Report shall be clearly marked with the SDG number, which is the sample number of the first sample in the SDG (as described in the following paragraph). This information shall be entered below the Lab Receipt Date on the TR. In addition, the TR for the last sample received in the SDG shall be clearly marked "SDG - FINAL SAMPLE."

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

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

C. Sample Data Package

The sample data package shall include data for analysis of all samples in one Sample Delivery Group (SDG), including but not limited to analytical samples, field samples, reanalyses, blanks, spikes, duplicates, laboratory control samples, and PE samples.

The sample data package shall be complete before submission, shall be consecutively paginated and shall include the following:

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

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

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

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

2. Sample Data

   Sample data shall be submitted with the Low Concentration Inorganic Analysis Data Reporting Forms for all samples in the SDG, including the PES, arranged in increasing alphanumeric EPA Sample Number order, followed by the QC analyses data, and Verification of Instrument Parameters forms, raw data, and copies of the preparation logs.

   a. Results -- Low Concentration Inorganics Analysis Data Sheet [FORM I - LCIN]

      Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and

release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot verify all data reported for each sample, he/she shall provide a detailed description of the problems associated with the sample(s) on the Cover Page.

The quantitative values shall be reported in units of micrograms per liter (ug/L) for all samples. No other units are acceptable. Analytical results shall be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10.

b. Quality Control Data

1) Initial and Continuing Calibration Verification [FORM II-LCIN]

2) CRDL Standards [FORM III-LCIN]

3) Linear Range Standards [FORM IV-LCIN]

4) Blanks [FORM V-LCIN]

5) ICP and ICP/MS Interference Check Sample [FORM VI-LCIN]

6) Spike Sample Recovery [FORM VII-LCIN]

7) Duplicates [FORM VIII-LCIN]

8) Laboratory Control Sample [FORM IX-LCIN]

9) Serial Dilution [FORM X-LCIN]

10) Standard Addition Results [FORM XI-LCIN]

11) Instrument Detection Limits [FORM XII-LCIN]

12) Interelement Correction Factors [FORM XIII-LCIN]

13) ICP/MS Tuning and Response Factor Criteria [FORM XIV-LCIN]

14) ICP/MS Internal Standards Summary [Form XV-LCIN]

15) Analysis Run Log (A) [FORM XVI-LCIN]

16) Analysis Run Log (B) [FORM XVII-LCIN]

17) Standard Solutions Sources [FORM XVIII-LCIN]

18) Sample Log-In Sheet [FORM DC-1]

19) Document Inventory Sheet [FORM DC-2]

c. Raw Data

For each reported value, the Contractor shall include in the data package all raw data from the instrument used to obtain that value and the QA/QC values reported (except for raw data for quarterly and annual verifications of instrument parameters). Raw data shall contain all instrument readouts used for the sample results, including those readouts that may fall below the IDL. All instruments shall provide a legible hard copy of the direct, real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy or other accurate facsimile of the direct sequential instrument readout shall be included.

The order of raw data in the data package shall be: ICP, ICP/MS, HYICP, Flame AA, Furnace AA, Mercury, Cyanide, Fluoride, and NO_2/NO_3-N. All raw data shall include intensities or concentration for ICP, ICP/MS, HYICP, absorbance or concentration for AA, spectrophotometric measurements, and millivolts for potentiometric measurements.

Raw data shall be labeled with EPA Sample Number and appropriate codes, specified in Table 1 Exhibit B, to unequivocally identify:

1) Calibration standards, including source and preparation date.

2) Initial and continuing calibration blanks and preparation blanks.

3) Initial and continuing calibration verification standards, interference check samples, CRDL standards, linear range standards, tuning standards, memory test standards and serial dilution samples.

4) Diluted and undiluted samples (by EPA Sample Number) and all dilutions and volumes used to obtain the reported values. (If the volumes and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters may be reported in the SDG Narrative).

5) Duplicates.

6) Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, a general statement outlining these parameters may be reported in the SDG Narrative).

7) Instrument used, any instrument adjustments, data corrections or other apparent anomalies in the measurement

record, including all data voided or data not used to obtain reported values and a brief written explanation in the SDG Narrative.

8) All information, for HYICP, Flame AA, and Furnace AA analysis, clearly and sequentially identified in the raw data, including EPA Sample Number and date of analysis, sample and analytical spike data, percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, slope and y intercept of linear fit, final sample concentration (standard addition concentration).

9) All ICP/MS tuning and mass calibration data, in addition to all internal standard results including the elements and concentration used.

10) All retention time data for Ion Chromatography.

11) Time and date of each and every analysis. Instrument run logs may be submitted if they contain this information. If the instrument does not automatically provide times of analysis, they shall be entered manually on all raw data for initial and continuing calibration verification and blanks, as well as on data for tuning solutions, CRDL standards, interference check samples and the linear range standard.

12) Integration times for all analyses.

d. Preparation Logs

Preparation Logs shall be submitted in the following order: ICP, ICP/MS, HYICP, Flame AA, Furnace AA, Mercury, Cyanide, Fluoride, and NO_2/NO_3-N. These logs shall include: (1) preparation date, (2) sample volume, (3) sufficient information to unequivocally identify which QC samples (i.e., laboratory control sample, preparation blank) correspond to each batch prepared, (4) comments describing any significant sample changes or reactions that occurred during preparation, and (5) report pH <2 or >12, as applicable.

3. A copy of the Sample Traffic Report and Cover Sheet submitted in Item C for all of the samples in the SDG. The Traffic Reports shall be arranged in increasing EPA Sample Number order, considering both alpha and numeric designations.

D. Data in Computer-Readable Form

The Contractor shall provide a computer-readable copy of the data on data reporting Forms I-XVIII for all samples in the Sample Delivery Group, as specified in the Contract Performance/Delivery Schedule. Computer-readable data deliverables shall be submitted on an IBM or IBM-compatible, 5.25 inch floppy double-sided, double density 360 K-byte or a high density 1.2 M-byte diskette or on an IBM or IBM-compatible, 3.5

inch double-sided, double density 720 K-byte or a high density 1.44 M-byte diskette. The data shall be recorded in ASCII, text file format, and shall adhere to the file, record and field specifications listed in Exhibit H.

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

E. Complete SDG File (CSF)

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

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

1. Original Sample Data Package (See Exhibit B, Item C)

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

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

   a. EPA Chain-of-Custody Record.

   b. Airbills.

   c. EPA (SMO) Traffic Reports.

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

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

   a. Form DC-1.

   b. Other receiving forms or copies of receiving logbooks.

   c. SDG Cover Sheet.

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

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

b. Internal sample and sample extract transfer chain-of-custody records.

c. All instrument output, including strip charts from screening activities.

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

a. Telephone contact logs.

b. Copies of personal logbook pages.

c. All handwritten Case-specific notes.

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

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

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

F. Quarterly/Annual Verification of Instrument Parameters

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

G. Results of Laboratory Control Sample (LCS)

Analytical results and QC for the method reference sample analysis, as specified in Exhibit E, shall be tabulated on Form IX.

H. Results of Performance Evaluation Sample (PES)

Analytical results for the PES analysis, as specified in Exhibit E, shall be tabulated on Form I.

Table 1

Codes for Labeling Data

Sample		XXXXXX
Duplicate		XXXXXXD
Matrix Spike		XXXXXXS
Serial Dilution		XXXXXXL
Analytical Spike		XXXXXXA
Post Digestion/Distillation Spike		XXXXXXA
MSA:		
Zero Addition		XXXXXX0
First Addition		XXXXXX1
Second Addition		XXXXXX2
Third Addition		XXXXXX3
Instrument Calibration Standards:		
ICP	S or S0 for blank standard	
Atomic Absorption and Cyanide	S0, S10,...etc.	
Initial Calibration Verification		ICV
Initial Calibration Blank		ICB
Continuing Calibration Verification		CCV
Continuing Calibration Blank		CCB
Interference Check Samples:		
Solution A		ICSA
Solution AB		ICSAB
CRDL Standard		CRI
Laboratory Control Samples		LCS
Preparation Blank		PBW
Linear Range Analysis Standard		LRS
Memory Test Solution		MTS
Tuning Solution		TS

Notes:

1. When an analytical spike or MSA is performed on samples other than field samples, the "A", "0", "1", "2" or "3" suffixes must be the last to be added to the EPA Sample Number. For instance, an analytical spike of a duplicate must be formatted "XXXXXXDA".

2. The numeric suffix that follows the "S" suffix for the standards indicates the true value of the concentration of the standard in ug/L.

3. ICP calibration standards usually consist of several analytes at different concentrations. Therefore, no numeric suffix can follow the ICP calibration standards unless all the analytes in the standard are prepared at the same concentrations. For instance, the blank for ICP must be formatted "S0".

SECTION III

FORM INSTRUCTION GUIDE

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

A. General Information and Header Information

B. Cover Page - [COVER PAGE - LCIN]

C. Analysis Data Sheet [FORM I - LCIN]

D. Initial and Continuing Calibration Verification [FORM II - LCIN]

E. CRDL Standards [FORM III - LCIN]

F. Linear Range Standards [FORM IV - LCIN]

G. Blanks [FORM V - LCIN]

H. ICP and ICP/MS Interference Check Sample [FORM VI- LCIN]

I. Spike Sample Recovery [FORM VII - LCIN]

J. Duplicates [FORM VIII - LCIN]

K. Laboratory Control Sample [FORM IX - LCIN]

L. Serial Dilution [FORM X - LCIN]

M. Standard Addition Results [FORM XI - LCIN]

N. Instrument Detection Limits [FORM XII - LCIN]

O. ICP and ICP/MS Interelement Correction Factors [FORM XIII - LCIN]

P. ICP and ICP/MS Tuning and Response Factor Criteria [FORM XIV - LCIN]

Q. ICP/MS Internal Standards Summary [FORM XV - LCIN]

R. Analysis Run Log (A) [FORM XVI - LCIN]

S. Analysis Run Log (B) [FORM XVII - LCIN]

T. Standard Solutions Sources [FORM XVIII - LCIN]

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

V. Document Inventory Sheet [Form DC-2]

A. General Information and Header Information

Values must be reported on the hardcopy data reporting forms according to the individual form instructions in this Section. Each form submitted must be filled out completely for all analytes and samples before proceeding to the next form of the same type. Multiple forms cannot be submitted in place of one form if the information on those forms can be submitted on one form.

All characters that appear on the data reporting forms presented in the contract (Exhibit B, Section IV) must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of SMO. The names of the various fields and analytes (i.e., "Lab Code", "Aluminum") must appear as they do on the forms in the contract, including the options specified in the form.

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

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

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

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

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

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

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

The other information common to several of the forms is the "EPA Sample No.". This number appears either in the upper right-hand corner of the

form, or as the left column of a table summarizing data from a number of samples. When "EPA Sample No." is entered into the triple-spaced box in the upper right-hand corner of a form, it must be centered on the middle line of the three lines that comprise the box.

All field samples and quality control samples must be identified with an EPA Sample Number. For field samples, the EPA Sample Number is the unique identifying number given in the Traffic Report that accompanied that sample. The quality control samples abbreviations listed in Table 1 must be used as appropriate.

The Form Suffix for each Form must appear in the two character space provided after the form number in the bottom section of the Form. The Form Suffix is used to sequentially distinguish between different forms of the same type (Form Number). No two Forms of the same type may have the same Form Suffix (see Exhibit H).

All the values substituted in the formulas given in the forms instructions must be exactly those values reported on the form for which the formula applies.

All results must be transcribed to Forms II-XVIII from the raw data to the specified number of decimal places that are described in Exhibit B and Exhibit H. The raw data result is to be rounded only when the number of figures in the raw data result exceeds the maximum number of figures specified for that result entry on 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 of floating decimal places are provided:

Raw Data Result	Specified Format	Correct Entry on Form
5.9	6.3 (to three decimal places)	5.900
5.99653	6.3 (to three decimal places)	5.997
95.99653	6.3 (to three decimal places)	95.997
995.99653	6.3 (to three decimal places)	996.00
9995.996	6.3 (to three decimal places)	9996.0
99995.9	6.3 (to three decimal places)	99996.
999995.9	6.3 (to three decimal places)	invalid

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

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

B. Cover Page [Cover Page - LCIN]

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

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

The "SOW No." is the SMO-designated number that indicates the version of the method under which analyses in the data package have been performed. For samples analyzed using this method, enter "10/91" for "SOW No."

Under "EPA Sample No.", enter the EPA Sample No. of each field sample, (including spikes, duplicates, and the PE sample) to eight spaces, 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 MAB123 is the lowest (considering both alpha and numeric characters) EPA Sample No. within the SDG, it would be entered in the first EPA Sample No. field. Samples would be listed below it, in ascending sequence - MAB124, MAB125, MAC111, MA1111, MA1111D, MA1111S, etc.

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

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

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

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

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

For "Name", enter the first and last name (to 25 spaces) of the person whose signature appears on the Cover Page.

For "Date", enter the date (formatted MM/DD/YY) on which the Cover Page is signed.

For "Title", enter the title (to 25 spaces) of the person whose signature appears on the Cover Page.

C. Analysis Data Sheet [Form I - LCIN]

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

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

For "Lab Sample ID", enter the laboratory sample ID for the EPA sample number listed on the form if one was designated, as listed on the Cover Page.

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

Under the column labeled "Concentration", enter for each analyte either the value of the result (if the concentration is greater than or equal to the Instrument Detection Limit), or the value of the Instrument Detection Limit for the analyte corrected for any dilutions (if the concentration is less than the Instrument Detection Limit).

Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the result value is greater than or equal to 10. NOTE: This requirement for reporting results to two or three significant figures applies to Form I-LCIN only. Follow the specific instructions for reporting all other results on required forms as described in this exhibit.

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

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

- C (Concentration) qualifier -- Enter "U" if the reported value was obtained from a reading that was less than the Instrument Detection Limit (IDL).
- Q qualifier -- Specified entries and their meanings are as follows:
  - E - The reported value is estimated because of the presence of interference.
  - 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.

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

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

o M (Method) qualifier -- Enter:

- "P " for ICP
- "M " for ICP/MS
- "H " for HYICP
- "F " for Graphite Furnace Atomic Absorption
- "A " for Flame Atomic Absorption
- "PM" for ICP when microwave digestion is used
- "MM" for ICP/MS when microwave digestion is used
- "HM" for HYICP when microwave digestion is used
- "FM" for Graphite Furnace AA when microwave digestion is used
- "AM" for Flame AA when microwave digestion is used
- "CV" for Cold Vapor AA
- "AV" for Automated Cold Vapor AA
- "AS" for Semi-Automated Spectrophotometric
- "C " for Manual Spectrophotometric
- "CA" for Medi-distillation Spectrophotometric
- "IC" for Ion Chromatography
- "AC" for Automated Spectrophotometric
- "IS" for Ion Selective Electrode (Potentiometric)
- "NR" if the analyte is not required to be analyzed
- " " if no results for the analyte appear on the form

A brief physical description of the sample before and after preparation must be reported in the fields for Color, Clarity, and Viscosity. The following descriptive terms are required:

Color	-	red, blue, yellow, green, orange, violet, white, colorless, brown, grey, or black
Clarity	-	clear, cloudy, or opaque
Viscosity	-	nonviscous or viscous

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

D. Initial and Continuing Calibration Verification [Form II - HCIN]

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

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

Under "WOMN", enter the number of the wavelength or mass number for which the results of each analyte are reported on the Form. The Wavelength or Mass Number is a number assigned to each wavelength (mass or detector configuration for ICP/MS) used when more than one wavelength

(mass or detector configuration for ICP/MS) 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. A mass number of "1" is assigned to the greatest mass or the most sensitive detector configuration of the same mass used for the analyte in the SDG. A mass number "2" is assigned to the second greatest mass or the less sensitive detector configuration of the same mass and so on. The field must be left blank if a single wavelength (or mass for ICP/MS) is used to obtain data for an analyte in the SDG.

Under "Initial Calibration True", enter the value (in ug/L, to two decimal places) of the concentration of each analyte in the Initial Calibration Verification Solution. If the analyte is not analyzed for, leave the field empty.

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

Under "Initial Calibration %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

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

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.

Under "Continuing Calibration True", enter the value (in ug/L, to two decimal place) of the concentration of each analyte in the Continuing Calibration Verification Solution. If the analyte is not analyzed for, leave the field empty.

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

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

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

Under "Continuing Calibration %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

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

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

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

If more than one wavelength or elemental expression is used to analyze an analyte, submit additional Forms II as appropriate.

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

In the case where more than one wavelength or elemental expression is used for an analyte in the SDG, all ICV and CCV results of the longest wavelength, greatest mass, or most sensitive detector configuration from all runs must be reported before proceeding to report the results of the second longest wavelength, the second greatest mass, or less sensitive detector configuration used, and so on.

E. <u>CRDL Standards</u> [Form III - LCIN]

This form is used to report analyte recoveries from analyses of the CRDL Standards.

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

Under "WOMN", enter the wavelength or mass number as explained in Part D.

Under "Initial True", enter the value (in ug/L, to two decimal places) of the concentration of each analyte in the CRDL Standard Source Solution that was analyzed for analytical samples associated with the SDG.

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

Under "Initial %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{CRDL Standard Initial Found}}{\text{CRDL Standard True}} \times 100$$

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

Under "Final %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{CRDL Standard Final Found}}{\text{CRDL Standard True}} \times 100$$

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

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

If more CRDL standards analyses were required or analyses were performed using more than one wavelength or elemental expression per analyte, submit additional Forms III in the order explained in Part D as appropriate.

The order of reporting CRDL standards for each analyte must follow the temporal order in which the standards were run starting with the first Form III and continuing to the following Forms III as appropriate. When multiple wavelengths or elemental expressions are used for one analyte, all the results of the longer wavelength or elemental expressions must be reported before proceeding to the next wavelength or elemental expression.

F. Linear Range Standards (LRS) [Form IV - LCIN]

This form is used to report analyte recoveries from analyses of the Linear Range Standards (LRS).

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

Under "WOMN", enter the wavelength or mass number as explained in Part D.

Under "Initial True", enter the value (in ug/L, to two decimal places) of the concentration of each analyte in the LRS Standard Source Solution that was analyzed for analytical samples associated with the SDG.

Under "Initial Found", enter the value (in ug/L, to three decimal places) of the concentration of each analyte measured in the LRS Standard Solution analyzed at the beginning of each run.

Under "Initial %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{LRS Standard Initial Found}}{\text{LRS Standard True}} \times 100$$

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

Under "Final %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{LRS Standard Final Found}}{\text{LRS Standard True}} \times 100$$

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

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

If more LRS standards analyses were required or analyses were performed using more than one wavelength or elemental expression per analyte, submit additional Forms IV in the order explained in Part D as appropriate.

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

G. **Blanks** [Form V - LCIN]

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

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

Under "WOMN", enter the wavelength or mass number as explained in Part A.

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

Under the "C" qualifier field, for any analyte enter "U" if the absolute value of the analyte in the blank is less than the IDL.

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

If only one Continuing Calibration Blank was analyzed, then leave the columns labeled "2" and "3" blank. If two additional 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 two Continuing Calibration Blanks were analyzed, then complete additional Forms V as appropriate.

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

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

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

If more than one wavelength or elemental expression is used to analyze an analyte, submit additional Forms V as appropriate.

The order of reporting ICBs and CCBs for each analyte must follow the temporal order in which the blanks were run starting with the first Form V and moving from left to right and continuing to the following Forms V as explained in Part D. When multiple wavelengths or elemental

expressions are used for the analysis of one analyte, all the results of the longer wavelength, greater mass, or more sensitive detector configuration must be reported before proceeding to the next wavelength or elemental expression.

H. ICP AND ICP/MS Interference Check Sample [Form VI - LCIN]

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

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

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

Under "WOMN", enter the wavelength or mass number as explained in Part D.

Under "True Sol. A", enter the true concentration (in ug/L, to two decimal places) of each analyte analyzed by ICP that is present in Solution A. A concentration of zero "0" must be entered for the analytes analyzed by ICP or ICP/MS that have no true value.

Under "True Sol. AB", enter the true concentration (in ug/L, to two decimal places) of each analyte present in Solution AB. A concentration of zero "0" must be entered for the analytes analyzed by ICP or ICP/MS that have no true value.

Under "Initial Found Sol. A", enter the concentration (in ug/L, to three decimal places) of each analyte analyzed by ICP that resulted from the initial analysis of Solution A as required in Exhibit E.

Under "Initial Found Sol. AB", enter the concentration (in ug/L, to three decimal places) of each analyte analyzed by ICP that resulted from the initial analysis of Solution AB as required in Exhibit E.

Under "Initial Found %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

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

Leave the field empty is True Solution AB is equal to zero.

Under "Final Found Sol. A", enter the concentration (in ug/L, to three decimal places) of each analyte analyzed by ICP that resulted from the final analysis of Solution A as required in Exhibit E.

Under "Final Found Sol. AB", enter the concentration (in ug/L, to three decimal places) of each analyte analyzed by ICP that resulted from the final analysis of Solution AB as required in Exhibit E.

Under "Final Found %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

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

Leave the field empty if True Solution AB is equal to zero.

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

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

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

If more ICS analyses were required, submit additional Forms VI as appropriate.

The order of reporting ICSs for each analyte must follow the temporal order in which the standards were run starting with the first Form VI and continuing to the following Forms VI as appropriate. When multiple wavelengths or elemental expressions are used for one analyte, all the results of longer wavelength, greater mass, or more sensitive detector configuration must be reported before proceeding to the next wavelength or elemental expression in the same manner as described in Part D.

I. <u>Spike Sample Recovery</u> [Form VII - LCIN]

This form is used to report results for the matrix spike.

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

In the "EPA Sample No." box, enter the EPA Sample Number (8 places maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box.

Under "WOMN", enter the wavelength or mass number as explained in Part D.

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

Under "Sample Result (SR)", enter the value (in ug/L, to three decimal places), of the concentration for each analyte in the sample (reported in the EPA Sample No. box) on which the matrix spike was performed. Enter the IDL value if the analyte was not detected. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

Under "Spiked Sample Result (SSR)", enter the value (in ug/L, to three decimal places), of the concentration for each analyte in the matrix spike sample. Enter the IDL value if the analyte was not detected. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

Under "Spike Added (SA)", enter the value (in ug/L, to three decimal places) of the concentration 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 ug/L.

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

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

%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 IDL.

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

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

If different samples were used for spike sample analysis of different analytes, additional Forms VII must be submitted for each sample as appropriate.

Use additional Forms VII for each sample on which a required spike sample analysis was performed.

J. Duplicates [Form VIII - LCIN]

The duplicates form is used to report results of duplicate analyses.

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

In the "EPA Sample No." box, enter the EPA Sample Number (8 places maximum) of the sample from which the duplicate results on this form were obtained. The number must be centered in the box.

Under "WOMN", enter the wavelength or mass number as explained in Part D.

Under "Control Limit", enter the numerical value of the IDL (in ug/L, to two decimal places) for the analyte if the sample or duplicate values were less than 5x IDL. If both the sample and duplicate values were less than the IDL or both were greater than or equal to 5x IDL, leave the field empty.

Under "Sample (S)", enter the original value (in ug/L, to three decimal places) of the concentration of each analyte in the sample (reported in the EPA Sample No. box) on which a duplicate analysis was performed. Enter the IDL value if the analyte was not detected. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample (S)" column.

Under "Duplicate (D)", enter the value (in ug/L, to three decimal places) of each analyte in the Duplicate sample (reported in the EPA Sample No. box). Enter the IDL value if the analyte was not detected. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Duplicate (D)" column.

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

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

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

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

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

Use additional Forms VIII for each sample on which a required duplicate sample analysis was performed.

K. <u>Laboratory Control Sample</u> [Form IX - LCIN]

This form is used to report results for the Laboratory Control Sample.

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

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.

Under "WOMN", enter the wavelength or mass number as explained in Part D.

Under "Limits", enter the lower limit (in ug/L, to two decimal places) in the left column, and the upper limit (in ug/L, to one decimal place) in the right column for each analyte in the LCS Source solutions.

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

Under "Found", enter the measured concentration (in ug/L, to three decimal places) of each analyte found in the LCS solutions. Enter the IDL value if the analyte was not detected.

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

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

$$\%R = \frac{\text{LCS Found}}{\text{LCS True}} \times 100$$

If the analyte concentration is less than the IDL, a value of zero must be substituted for the LCS found.

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

Submit additional Forms IX as appropriate, if more than one LCS was required. In addition, submit additional Forms IX if more than one wavelength, mass, or method was used to determine an analyte for a sample, as described in Part D:

L. <u>Serial Dilution</u> [Form X - LCIN]

The Serial Dilution Form is used to report results of serial dilution analyses.

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

In the "EPA Sample No." box, enter the EPA Sample Number (8 places maximum) of the sample from which the duplicate results on this form were obtained. The number must be centered in the box.

Under "WOMN", enter the wavelength or mass number as explained in Part D.

Under "Initial Sample Result (I)", enter the measured value (in ug/L, to three decimal places) of the concentration of each analyte in the undiluted sample (reported in the EPA Sample No. box) on which a Serial Dilution analysis was performed. Enter the IDL value if the analyte

was not detected. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Initial Sample Result (I)" column.

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

Under "Serial Dilution Result (S)", enter the measured concentration value (in ug/L, to three decimal places) of each analyte in the serially diluted sample (reported in the EPA Sample No. box). Enter the IDL value multiplied by five if the analyte was not detected. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Serial Dilution Result (S)" column.

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

Under "% Difference", enter the absolute value (to the nearest whole number) of the percent difference in concentration of required analytes, between the initial sample and the diluted sample (adjusted for dilution) for all analytes detected above the IDL in the sample, computed according to the following equation:

$$RPD = \frac{|I - S|}{I} \times 100$$

A value of zero must be substituted for S if the analyte concentration is less than the IDL. If the analyte concentration is less than the IDL in I, leave the "% Difference" field empty.

Under "Q", enter "E" if the % difference value is greater than 10% and the original sample concentration reported on Form I is greater than 50 times the IDL.

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

Use additional Forms X for each sample on which a required serial dilution analysis was performed.

M. <u>Standard Addition Results</u> [Form XI - LCIN]

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

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

Under "EPA Sample No.", enter the EPA Sample Numbers (8 places maximum) of all analytical samples analyzed using MSA. This includes reruns by MSA (if the first MSA was out of control) as explained in Exhibit E.

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

Under "An", enter the chemical symbol (3 spaces maximum) for each analyte for which MSA was required for each sample listed. The analytes must be in alphabetic listing of the chemical symbols.

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

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

Under "First Added" (x_2), enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the first addition to the sample analyzed by MSA.

Under "First Found" (y_2), enter the measured value in absorbance or intensity units (to two decimal places) for the analyte in the sample solution spiked with the first addition.

Under "Second Added" (x_3), enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the second addition to the sample analyzed by MSA.

Under "Second Found" (y_3), enter the measured value in absorbance or intensity units (to three decimal places) for the analyte in the sample solution spiked with the second addition.

Under "Third Added" (x_4), enter the final concentration in ug/L (to three decimal places) of the analyte (excluding sample contribution) after the third addition to the sample analyzed by MSA.

Under "Third Found" (y_4), enter the measured value in absorbance or intensity units (to three decimal places) for the analyte in the sample solution spiked with the third addition.

Note that "Zero Found", "First Found", "Second Found", and "Third Found" must have the same dilution factor.

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

Final Conc. = - (x-intercept)

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

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").

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

$$r = \frac{4 \sum x_i y_i - \sum x_i \sum y_i}{[4 \sum x_i^2 - (\sum x_i)^2]^{1/2} [4 \sum y_i^2 - (\sum y_i)^2]^{1/2}}$$

Where, $x_i = 0$

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.

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

N. Instrument Detection Limits [Form XII - LCIN]

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

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

Enter the "Instrument ID Number" for each instrument used to produce data for the SDG, as explained in Section H.

For "Method", enter the method of analysis as explained in Part C.

Enter the date (formatted MM/DD/YY) on which the IDL values were determined for use. This date must not exceed any of the analysis dates for that instrument in the SDG data package. Also, it must not precede them by more than three calendar months.

Under "Wavelength or Mass Number (WOMN)", enter the wavelength or mass number, as explained in Part D.

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

Under "Mass", enter the mass to charge ratio (m/z, nominal unit mass) for each analyte for which an Instrument Detection Limit (IDL) has been

established and is listed in the IDL column. If more than one mass to charge ratio is used in the elemental expression to provide quantitation, then the mass to charge ratio listed should be the analyte's primary mass in the equation used for quantitation. For example, if the elemental expression for the first selenium (WOMN) is Se = (1.0000)(m/z 78)-(0.1869)(m/z 76) then the mass reported should be 78. If more than one mass to charge ratio is used for an analyte, use additional Forms XII as appropriate to report the Instrument Detection Limit.

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

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

Under "CRDL", enter the Contract Required Detection Limit (in ug/L), as established in Exhibit C. If detection limits other than those listed in Exhibit C were required such as in SAS analysis, those detection limits become the CRDL. They must be reported on this form and used anywhere else where CRDL is referenced.

Under "IDL", enter the Instrument Detection Limit (in ug/L) as determined by the laboratory for each analyte analyzed by the instrument for which the ID Number is listed on this form. IDLs must be reported to <u>two</u> significant figures if the IDL value is less than <u>100</u> and to <u>three</u> significant figures for values above or equal to <u>100</u>.

Use additional Forms XII if more instruments, wavelengths, or elemental expressions are used.

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

O. <u>ICP and ICP/MS Interelement Correction Factors</u> [Form XIII-LCIN]

This form documents for each ICP and ICP/MS instrument the interelement correction factors applied by the Contractor to obtain data for the SDG.

Although the correction factors are determined annually (every 12 calendar months), a copy of the results of the annual interelement correction factors must be included with each SDG data package on Form XIII.

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

Enter the "Instrument ID Number" for each ICP and ICP/MS instrument used to produce data for the SDG, as explained in Section H. If more than one ICP instrument is used, submit additional Forms XIII as appropriate.

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

Report the date (formatted as MM/DD/YY) on which these correction factors were determined for use. This date must not exceed any of the analysis dates reported for that instrument in the SDG data package. Also, it must not precede them by more than 12 calendar months.

Under "Wavelength or Mass", list the wavelength (in nanometers, to two decimal places) for ICP instruments, or the mass to charge ratio (m/z, to nominal unit mass) for ICP/MS instruments for each analyte analyzed by either one of the two instruments. If more than one wavelength or mass is used, submit additional Forms XIII as appropriate.

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.

In the column, enter the correction factor (negative, positive or zero, to seven decimal places, 10 spaces 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.

Use additional Forms XIII as appropriate if correction factors for more than five analytes were applied.

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

P. <u>ICP and ICP/MS Tuning and Response Factor Criteria</u> [Form XIV - LCIN]

This form is used for reporting tuning, response factor, and mass calibration verification results for each ICP/MS run used to report data in the SDG.

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

Enter the "Instrument ID Number" for the ICP/MS instrument used to produce data on the form, as explained in Section H. A Form XIV must be submitted for each ICP/MS analysis run in the SDG.

For "Run No.", enter the run number (two spaces maximum) from which the information on the form was taken. The run number is a sequential number for each instrument in the SDG that identifies the different analytical runs that are performed on the same instrument. The first run number for an instrument must be one, the second must be two, and so on.

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

For "Analysis Date", enter the date (formatted MM/DD/YY) of analysis of the initial tuning solution from which the information on the form was taken.

For "Analysis Times, Initial", enter the time (in military format - HHMM) of analysis of the initial tuning solution from which the information on this form was taken.

For "Analysis Times, Final", enter the time (in military format - HHMM) of analysis of the final tuning solution from which the information on this form was taken.

Under "% Relative Abundance, Initial", enter the percent relative abundance (to two decimal places) calculated from the intensities measured, for each of the isotopes listed, as a result of analyzing the 100 ppb tuning solution at the beginning of each ICP/MS run. The isotopes are listed in the first column from the left in the Tuning Section of the Form.

Under "% Relative Abundance, Final", enter the percent relative abundance (to two decimal places) calculated from the intensities measured, for each of the isotopes listed, as a result of analyzing the 100 ppb tuning solution at the end of each ICP/MS run. The isotopes are listed in the first column from the left in the Tuning Section of the Form.

Under "Response Factor, Initial", enter the value for the measured response factor (in counts per second, to the nearest whole number) in the 100 ppb tuning solution analyzed at the beginning of each ICP/MS run, for each mass to charge ratio listed in the first column from the left in the Response Factor Section of the Form.

Under "Response Factor, Final", enter the value for the measured response factor (in counts per second, to the nearest whole number) in the 100 ppb tuning solution analyzed at the end of each ICP/MS run for each mass to charge ratio listed in the first column from the left in the Response Factor Section of the Form.

Under "Observed Mass", enter the observed mass (to nominal unit mass) in the 100 ppb tuning solution analyzed at the beginning of each ICP/MS run for each mass to charge ratio listed in the first column from the left in the Mass Calibration Section of the Form.

The values measured and reported in the Tuning, Response Factor, and Mass Calibration Sections of the Form must be within the control limits listed in the second column from the left in each of the Sections.

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

If more tuning solutions analyses were required, submit additional Forms XIV in the order explained in Part D as appropriate.

The order of reporting the tuning solution results must follow the temporal order in which the solutions were run starting with the first Form XIV and continuing to the following Form XIV, as appropriate.

Q. ICP/MS Internal Standards Summary [Form XV-LCIN]

This form is used to report the internal standards intensity levels for ICP/MS. The relative intensity of each of the internal standards in all analyses performed on each ICP/MS must be reported on the form.

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

All field samples and all quality control analyses (including tuning solutions, calibration standards, ICVs, CCVs, ICBs, CCBs, MTS, CRIs, ICSs, LRSs, LCSs, PBs, duplicates, PE Samples, and spikes) associated with the SDG must be reported on Form XV. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

Submit one Form XV 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 Forms XV as appropriate. Each new run must be started on the first line of Form XV.

An identical number of Forms XVI with ICP/MS methods and Forms XV must exist.

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

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

For "Run No.", enter the run number as explained in Part P.

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

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

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

Under "EPA Sample No.", enter the EPA sample number of each analysis,

including all QC operations applicable to the SDG (formatted according to Table 1, Exhibit B). All EPA sample numbers must be listed in increasing temporal (date and time) order of analysis, continuing to the next Form XV for the instrument run if applicable. The analysis date and time of other analyses not associated with the SDG, but analyzed by the instrument in the reported analytical run, must be reported. Those analyses must be identified with the EPA Sample No. of "ZZZZZZ". Samples identified as "ZZZZZZ" need not have intensities reported for internal standards.

Under "Time", enter the time (in military format - HHMM) at which each analysis was performed.

For any particular ICP/MS run, the EPA Sample No. and time sequence on Form XV and XVI must be identical.

Under "Internal Standards %D For:", enter the chemical symbol of the internal standard in the two-space header field provided to indicate the internal standard for which the percent differences in that column were reported.

In the column, enter the percent relative intensity (to the nearest whole number) of the intensity of the internal standard in the EPA Sample Number for each sample analysis listed on the form (excluding "ZZZZZZ") and the intensity of the internal standard in the blank calibration standard (SO). The percent relative intensity (%R) is calculated using the following formula:

$$\%R = \frac{SOI}{SI} \times 100$$

Where, the SOI is the intensity of the internal standard in the blank calibration standard, and SI is the intensity of internal standard in the EPA Sample No. in the same units.

Under the "Q" column to the right of each %R column, enter an "E" if the %R for a field sample, PES, duplicate, or spike is less than 30% or greater than 125% for the second time after being run at a five-fold dilution. If the percent relative intensity is greater than 30% and less than 125%, then leave the field empty.

Columns of internal standard %R must be entered left to right starting with the internal standards of the lower mass on the first Form XV and proceeding to the following Form XV as appropriate.

R. <u>Analysis Run Log (A)</u> [Form XVI-LCIN]

This form is used to report the sample analysis run log for ICP and ICP/MS only. In addition, the samples reported on this form must have been prepared in the same manner using no pre-preparation dilution or concentration steps. The results reported on Form I for the samples listed on this form for each analyte must be obtained by multiplying each analyte's concentration (in ug/L) from the instrument by the dilution factor listed on the form.

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

All field samples and all quality control analyses (including tuning solutions, ICP serial dilutions, calibration standards, ICVs, CCVs, ICBs, CCBs, MTS, CRIs, ICSs, LRSs, LCSs, PBs, duplicates, PE samples, and spikes) associated with the SDG must be reported on Form XVI. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

Submit one Form XVI 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 Forms XVI as appropriate.

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

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

For "Run No.", enter the run number as explained in Part P.

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

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

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

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

Under "Prep. Batch Number", enter the preparation batch number for each sample and quality control sample preparation (including duplicates, spikes, LCSs, PBs, and PE samples) that are reported on the Form. The preparation batch number is used to link the sample analysis with the appropriate preparation batch. It consists of an ordered combination of the date of preparation (formatted MMDDYY), the hour of preparation (in military format - HH), and the method of preparation. The preparation batch number must be left justified and may not have any blank spaces

between its components. It may not have more than one leading blank. Single digit hours and months must be padded to the left with zeros. The following are examples of preparation batch numbers:

Prep. Batch Number	Hour	Preparation Date	Method
"11308915CV"	15	11/30/89	CV
"11038915P "	15	11/30/89	P
"01029008F "	8	01/01/90	F
"12908F "	invalid		

Under "Time", enter the time (in military format - HHMM) at which each analysis was performed.

Note that for a particular sample a dilution factor of "1" must be entered if the preparation product was analyzed without adding any further volume of dilutant or any other solutions to the sample or an aliquot of that sample taken for preparation.

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

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

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 on any of the forms in the SDG. Leave the column empty for each analyte if the analysis was not used to report the particular analyte.

S. Analysis Run Log (B) [Form XVII-LCIN]

This form is used to report the sample analysis run log for each instrument used for analysis in the SDG. This includes ICP and ICP/MS analysis runs where conditions for reporting on Form XVI were not met. Form XVII is analyte and method specific.

A run is defined as the continuous totality of analyses performed by an instrument throughout the sequence initiated by, and including, the

initial and the final tuning solution, the first required calibration standard and terminated by, and including, the continuing calibration verification and blank following the last required analytical sample.

All field samples and all quality control analyses (including tuning solutions, serial dilutions, calibration standards, ICVs, CCVs, ICBs, CCBs, MTS, CRIs, ICSs, LRSs, LCSs, PBs, duplicates, PE Samples, matrix spikes, analytical spikes, and each addition analyzed for MSA determination) associated with the SDG must be reported on Form XVII. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

Submit one Form XVII 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 Forms XVII as appropriate.

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

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

For "Run No.", enter the run number as explained in Part P.

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

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

For "Analyte", enter the analyte's chemical symbol (three spaces maximum) for which the analysis run is being reported on the Form. Submit a Form XVII for each analyte analyzed.

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

For "Retention Time Window", enter the retention time window (in seconds, to two decimal places) established for the column used for analysis of the analyte on this form if the method used is "IC".

For the "Lower Limit", enter the retention time lower limit (in seconds, to two decimal places) for the ion chromatography (IC) column used for analysis on this form.

For the "Upper Limit", enter the retention time upper limit (in seconds, to two decimal places) for the Ion Chromatography (IC) column used for analysis on this form.

Note that the difference between the "Upper Limit" and "Lower Limit" of the retention time must equal the "Retention Time Window". If the method reported on this form is not "IC", leave the "Retention Time Window", "Lower Limit", and "Upper Limit" fields blank.

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

Under "Prep. Batch Number", enter the preparation batch number as explained in Part R.

Under "Inl. Vol.", enter the initial volume (in mL, to the nearest whole number) of each sample or aliquot of the sample taken for preparation (distillation, digestion, etc.) for analysis by the method indicated in the header section of the Form. This field must have a value for each field sample listed.

Under "Fin. Vol.", 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 field sample listed.

Under "Time", enter the time (in military format - HHMM) at which each analysis was performed.

Under "D/F", enter the dilution factor (to two decimal places) by which the final product of preparation procedure (digestate or distillate) needed to be diluted for each analysis performed.

Note that for a particular sample, a dilution factor of "1" must be entered if the preparation product was analyzed without adding any further volume of dilutant or any other solution to the "Fin. Vol." of the sample or an aliquot of that "Fin. Vol." listed for that sample on this form.

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

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

Under "%R", enter the percent recovery (to two decimal places) for each analytical spike analyzed. Leave the field blank if the analysis reported is not an analytical spike. A %R of "-9999" must be entered for the analytical spike if either the sample or the analytical spike result is greater than the calibration range of the instrument.

Under "%RSD", enter the relative standard deviation of the replicate exposures or injections for each analysis reported on this form.

Under "Retention Time", enter the retention time (in seconds, to two decimal places) for each analysis reported on this form. The retention time must be within the lower and upper limits reported on the Form. Leave the field blank If the method reported on the form is not "IC".

T. Standard Solutions Sources [Form XVIII-LCIN]

This form is used to report the source of each standard solution on an analyte-by-analyte basis used for initial and continuing calibration verifications, CRDL, LRS, ICS, and LCS standards used as a QC analysis in the SDG.

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

Under "ICV Standard Source", enter the initial calibration source (10 spaces maximum) for each analyte for which ICV results were reported on Form II. For supplied solutions, entering "SMO" is not sufficient. Supplied solutions must be identified using the codes supplied with the solutions for identification. For solutions that are not provided, enter sufficient information in the available 12 spaces to unequivocally identify the manufacturer and the solution used.

Under "CCV Standard Source", enter the continuing calibration source (10 spaces maximum) for each analyte for which CCV results were reported on Form II, as described for the initial calibration source.

Under "CRI Standard Source", enter the CRDL standard source (10 spaces maximum) for each analyte for which CRDL standard results were reported on Form III, as described for the initial calibration source.

Under "LRS Standard Source", enter the Linear Range Analysis source (10 spaces maximum) for each analyte for which LRS standard results were reported on Form IV, as described for the initial calibration source.

Under "ICS Standard Source", enter the ICP and ICP/MS Interference source (10 spaces maximum) for each analyte for which ICS standard results were reported on Form VI, as described for the initial calibration source.

Under "LCS Standard Source", enter the Laboratory Control Sample source (10 spaces maximum) for each analyte for which LCS standard results were reported on Form IX, as described for the initial calibration source.

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

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

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

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

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

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

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

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

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

V. Document Inventory Sheet (Form DC-2)

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

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

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

SECTION IV

DATA REPORTING FORMS

LOW CONCENTRATION INORGANICS

COVER PAGE

Lab Name: _____ Contract: _____

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

SOW No.: ____

EPA Sample No.	Lab Sample ID.

		ICP	ICP/MS
Were ICP and ICP/MS interelement corrections applied?	(Yes/No)	___	___
Were ICP and ICP/MS background corrections applied?	(Yes/No)	___	___
If yes, were raw data generated before application of background corrections?	(Yes/No)	___	___

Comments:

_____

_____

_____

_____

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

Signature: _____ Name: _____

Date: _____ Title: _____

LOW CONCENTRATION INORGANICS

ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

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

Lab Sample ID: _____ Date Received: _____

Concentration Units: ug/L

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				
7440-47-3	Calcium				
7440-70-2	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				
7440-02-7	Potassium				
7440-02-0	Nickel				
7782-49-2	Selenium				
7440-22-4	Silver				
7440-23-5	Sodium				
7440-28-0	Thallium				
7440-62-2	Vanadium				
7440-66-6	Zinc				
	Cyanide				
1698-44-88	Fluoride				
	NO2/NO3-N				

	Color	Clarity	Viscosity
Before:	_____	_____	_____
After:	_____	_____	_____

Comments:

_____

_____

_____

_____

FORM I __ - LCIN 10/91

LOW CONCENTRATION INORGANICS

INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: _____ Contract: _____

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

Run No.: ___

Concentration Units: ug/L

Analyte	WOMN	Initial Calibration			Continuing Calibration					M
		True	Found	%R	True	Found 1	%R 1	Found 2	%R 2	
Aluminum										
Antimony										
Arsenic										
Barium										
Beryllium										
Cadmium										
Calcium										
Chromium										
Cobalt										
Copper										
Iron										
Lead										
Magnesium										
Manganese										
Mercury										
Nickel										
Potassium										
Selenium										
Silver										
Sodium										
Thallium										
Vanadium										
Zinc										
Cyanide										
Fluoride										
NO2/NO3-N										

Comments:

_____

_____

_____

_____

LOW CONCENTRATIQN INORGANICS

CRDL STANDARDS

Lab Name: _____ Contract: _____

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

Run No.: ___

Concentration Units: ug/L

Analyte	WOMN	Initial			Final		M
		True	Found	%R	Found	%R	
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Mercury							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							
Cyanide							
Fluoride							
NO2/NO3-N							

Comments:

_____

_____

_____

_____

LOW CONCENTRATION INORGANICS

LRS

Lab Name: _____ Contract: _____

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

Run No.: ___

Concentration Units: ug/L

Analyte	WOMN	Initial			Final		M
		True	Found	%R	Found	%R	
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Mercury							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							
Cyanide							
Fluoride							
NO2/NO3-N							

Comments:

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LOW CONCENTRATION INORGANICS

BLANKS

Lab Name: _____ Contract: _____

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

Run No.: ___

Concentration Units: ug/L

Analyte	WOMN	Initial Calib. Blank	C	Continuing Calibration Blanks 1	C	2	C	3	C	Prep. Blank	C	M
_____	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Aluminum_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Antimony_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Arsenic__	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Barium___	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Beryllium	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Cadmium__	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Calcium__	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Chromium_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Cobalt___	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Copper___	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Iron____	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Lead____	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Magnesium	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Manganese	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Mercury__	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Nickel___	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Potassium	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Selenium_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Silver___	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Sodium___	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Thallium_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Vanadium_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Zinc____	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Cyanide__	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
Fluoride_	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
NO2/NO3-N	_	_____	_	_____	_	_____	_	_____	_	_____	_	_
_____	_	_____	_	_____	_	_____	_	_____	_	_____	_	_

Comments:

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LOW CONCENTRATION INORGANICS

ICS

Lab Name: _____ Contract: _____

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

Instrument ID Number: _____ Run No.: ___

Concentration Units: ug/L

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

Comments:

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FORM VI __ - LCIN 10/9

LOW CONCENTRATION INORGANICS

SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

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

Concentration Units: ug/L

Analyte	WOMN	Control Limit %R	Sample Result (SR)	C	Spiked Sample Result (SSR)	C	Spike Added (SA)	%R	Q	M
Aluminum										
Antimony										
Arsenic										
Barium										
Beryllium										
Cadmium										
Calcium										
Chromium										
Cobalt										
Copper										
Iron										
Lead										
Magnesium										
Manganese										
Mercury										
Nickel										
Nickel										
Selenium										
Silver										
Sodium										
Thallium										
Vanadium										
Zinc										
Cyanide										
Fluoride										
NO2/NO3-N										

Comments:

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FORM VII __ - LCIN

10/91

LOW CONCENTRATION INORGANICS

DUPLICATES

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

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

Concentration Units: ug/L

Analyte	WOMN	Control Limit	Sample (S)	C	Duplicate (D)	C	RPD	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									
Fluoride									
NO2/NO3-N									

Comments:

_____

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FORM VIII __ - LCIN 10/91

LOW CONCENTRATION INORGANICS

LCS

Lab Name: _____ Contract: _____

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

Concentration Units: ug/L

Analyte	WOMN	Limits Lower	Limits Upper	True	Found	C	%R	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								
Fluoride								
NO2/NO3-N								

Comments:

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LOW CONCENTRATION INORGANICS

SERIAL DILUTION

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

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

Concentration Units: ug/L

Analyte	WOMN	Initial Sample Result (I)	C	Serial Dilution Result (S)	C	% Difference	Q	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								
Fluoride								
NO2/NO3-N								

Comments:

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FORM X __ - LCIN 10/91

LOW CONCENTRATION INORGANICS

STANDARD ADDITION RESULTS

Lab Name: ____________________ Contract: ________

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

Concentration Units: ug/L

EPA Sample No.	An	ADDITIONS Zero	First		Second		Third		Final Conc.	r	Q	M
		Found	Added	Found	Added	Found	Added	Found				

FORM XI __ - LCIN 10/91

LOW CONCENTRATION INORGANICS

IDL

Lab Name: _____ Contract: _____

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

Instrument ID Number: _____ Method: __ Date: _____

Concentration Units: ug/L

Analyte	Wavelength or Mass Number (WOMN)	Wave-Length (nm)	Mass (m/z)	Integ. Time (sec)	Back-ground	CRDL	IDL
Aluminum						100	
Antimony						5	
Arsenic						2	
Barium						20	
Beryllium						1	
Cadmium						1	
Calcium						500	
Chromium						10	
Cobalt						10	
Copper						10	
Iron						100	
Lead						2	
Magnesium						500	
Manganese						10	
Mercury						0.2	
Nickel						20	
Potassium						750	
Selenium						3	
Silver						10	
Sodium						500	
Thallium						10	
Vanadium						10	
Zinc						20	
Cyanide						10	
Fluoride						200	
NO2/NO3-N						100	

Comments:

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LOW CONCENTRATION INORGANICS

INTERELEMENT CORRECTION FACTORS

Lab Name: _____ Contract: _____

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

Instrument ID Number: _____ Method: __ Date: _____

Analyte	Wave-Length or Mass	Interelement Correction Factors for:				
		___	___	___	___	___
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

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LOW CONCENTRATION INORGANICS

ICP/MS TUNING AND RESPONSE FACTOR CRITERIA

Lab Name: _____ Contract: _____

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

Instrument ID Number: _____ Run No.: __ Method: __

Analysis Date: _____ Analysis Times: (initial) _____ (Final) _____

Tuning

m/z	Ion Abundance Criteria	% Relative Abundance	
		Initial	Final
7Li/59Co	(0.20 - 1.00)		
59Co/59Co	(1.00)		
115In/59Co	(0.75 - 2.00)		
205Tl/59Co	(0.50 - 1.20)		

Response Factor (counts per second)

m/z	Response Factor Criteria	RF100 (1) Response	
		Initial	Final
7Li	(> 2,000)		
59Co	(>20,000)		
115In	(>10,000)		
102Ru	(< 25)		
205Tl	(> 1,000)		

(1) Background (RF0) for 102Ru

Mass Calibration

m/z	Acceptable Mass Range	Observed Mass
7Li	(6.9160 - 7.1160)	
59Co	(58.8332 - 59.0332)	
115In	(114.8040 - 115.0040)	
205Tl	(204.8744 - 205.0744)	

LOW CONCENTRATION INORGANICS

ICP/MS INTERNAL STANDARDS SUMMARY

Lab Name: ____________________ Contract: ________

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

Instrument ID Number: ____________ Run No.: __ Method: __

Start Date: ________ End Date: ________

EPA Sample No.	Time	Internal Standards %R For:									
		__	Q	__	Q	__	Q	__	Q	__	Q

FORM XV __ - LCIN 10/91

LOW CONCENTRATION INORGANIC

ANALYSIS RUN LOG (A)

Lab Name: ______________________ Contract: ________

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

Instrument ID Number: ____________ Run No.: __ Method: __

Start Date: ________ End Date: ________

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

FORM XVI __ - LCIN 10/91

LOW CONCENTRATION INORGANICS

ANALYSIS RUN LOG (B)

Lab Name: ____________________ Contract: ________

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

Instrument ID Number: ____________ Run No.: __ Method: __

Start Date: ________ Analyte: __ End Date: ________

Retention Time Window: ______ Lower Limit: ______ Upper Limit: _____

EPA Sample No.	Prep. Batch Number	Inl. Vol.	Fin. Vol.	Time	D/F	%R	%RSD	Retention Time

FORM XVII __ - LCIN 10/91

SAMPLE LOG-IN SHEET

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

Remarks:

1. Custody Seal(s) — Present/Absent* Intact/Broken
2. Custody Seal Nos.: ______
3. Chain-of-Custody Records — Present/Absent*
4. Traffic Reports or Packing Lists — Present/Absent*
5. Airbill — Airbill/Sticker Present/Absent*
6. Airbill No.: ______
7. Sample Tags — Present/Absent*

   Sample Tag Numbers — Listed/Not Listed on Chain-of-Custody
8. Sample Condition: Intact/Broken*/Leaking
9. Does information on custody records, traffic reports, and sample tags agree? Yes/No*
10. Date Received at Lab: ______
11. Time Received: ______

EPA Sample #	Corresponding Sample Tag #	Corresponding Assigned Lab #	Remarks: Condition of Sample Shipment, etc.

Sample Transfer

Fraction	Fraction
Area #	Area #
By	By
On	On

* Contact SMO and attach record of resolution.

Received By	Logbook No
Date	Logbook Page No.

FORM DC-1

LOW CONCENTRATION WATER FOR 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. _____

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

		Page Nos.		(Please Check:)	
		From	To	Lab	Region
1.	Inventory Sheet (DC-2) (Do not number)			___	___
2.	Cover Page	___	___	___	___
3.	Inorganic Analysis Data Sheet (Form I)	___	___	___	___
4.	Initial & Continuing Calibration Verification (Form II - LCIN)	___	___	___	___
5.	CRDL Standards (Form III - LCIN)	___	___	___	___
6.	Linear Range Standards (Form IV-LCIN)	___	___	___	___
7.	Blanks (Form V-LCIN)	___	___	___	___
8.	ICP & ICP/MS Interference Check Sample (Form VI-LCIN)	___	___	___	___
9.	Spike Sample Recovery (Form VII-LCIN)	___	___	___	___
10.	Duplicates (Form VIII-LCIN)	___	___	___	___
11.	Lab Control Sample (Form IX-LCIN)	___	___	___	___
12.	Serial Dilution (Form X-LCIN)	___	___	___	___
13.	Standard Addition Results (Form XI-LCIN)	___	___	___	___
14.	Instrument Detection Limits (Form XII-LCIN)	___	___	___	___
15.	Interelement Correction Factor (Form XIII-LCIN)	___	___	___	___
16.	ICP/MS Tuning & Response Factor Criteria (Form XIV-LCIN)	___	___	___	___
17.	ICP/MS Internal Standards Summary (Form XV-LCIN)	___	___	___	___
18.	Analysis Run Log (A) (Form XVI-LCIN)	___	___	___	___
19.	Analysis Run Log (B) (Form XVII-LCIN)	___	___	___	___
20.	Standard Solutions Sources (Form XVIII-LCIN)	___	___	___	___
21.	ICP Raw Data	___	___	___	___
22.	ICP/MS Raw Data	___	___	___	___
23.	HYICP Raw Data	___	___	___	___
24.	Furnace AA Raw Data	___	___	___	___

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

36. Comments:

_____

_____

Completed by (CLP Lab):

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

Audited by (EPA):

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

EXHIBIT C

TABLES

TABLE I
INORGANIC TARGET ANALYTE LIST (TAL)

Analyte	Contract Required Detection Limit (1,2) (ug/L)
Aluminum	100
Antimony	5
Arsenic	2
Barium	20
Beryllium	1
Cadmium	1
Calcium	500
Chromium	10
Cobalt	10
Copper	10
Iron	100
Lead	2
Magnesium	500
Manganese	10
Mercury	0.2
Nickel	20
Potassium	750
Selenium	3
Silver	10
Sodium	500
Thallium	10
Vanadium	10
Zinc	20
Cyanide	10
Fluoride	200
NO_2/NO_3-N	100

(1) Any analytical method specified in Exhibit D may be utilized-, except for the ICP/MS method (see Table II) and the IC method for Fluoride, provided the documented instrument detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

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

For lead:

Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 220
Contract Required Detection Limit (CRDL) = 2

The value of 220 may be reported even though instrument detection limit is greater than CRDL. The instrument detection limit must be documented as described in Exhibit E.

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

TABLE II
INORGANIC TARGET ANALYTE LIST (TAL)
FOR ICP/MS ANALYSES

Analyte	Contract Required Detection Limit (1,2) (ug/L)
Aluminum	100
Antimony	5
Arsenic	2
Barium	20
Beryllium	1
Cadmium	1
Chromium	10
Cobalt	10
Copper	10
Iron	100
Lead	2
Manganese	10
Nickel	20
Selenium	3
Silver	10
Thallium	10
Vanadium	10
Zinc	20

(1) The ICP/MS method specified in Exhibit D may be utilized provided the documented instrument detection limits meet the Contract Required Detection Limit (CRDL) requirements.

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

TABLE III
INITIAL AND CONTINUING CALIBRATION VERIFICATION,
CRDL STANDARD CONTROL LIMITS, AND LCS STANDARD CONTROL LIMITS
FOR INORGANIC ANALYSES

INITIAL AND CONTINUING CALIBRATION VERIFICATION LIMITS			
		% of True Value (EPA Set)	
Analytical Method	Inorganic Species	Low Limit	High Limit
ICP/AA	Metals	90	110
ICP/MS	Metals	90	110
ICP/HYDRIDE.	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115
Other	Fluoride	85	115
Other	NO_2/NO_3-N	90	110

CRDL STANDARD CONTROL LIMITS			
		% of True Value (EPA Set)	
Analytical Method	Inorganic Species	Low Limit	High Limit
ICP/OES and AA	Metals	50	150
ICP/MS	Metals	50	150
ICP/HYDRIDE	Metals	50	150
Cold Vapor AA	Mercury	50	150
Other	Cyanide	50	150
Other	Fluoride	50	150
Other	NO_2/NO_3-N	50	150

LCS STANDARD CONTROL LIMITS

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

TABLE IV
SPIKING LEVELS FOR MATRIX SPIKE(1)

Element	Water (ug/L)
Aluminum	500
Antimony	50(2)
Arsenic	10(3)
[illegible]	200
Beryllium	10
Cadmium	10
Calcium	*
Chromium	50
Cobalt	100
Copper	50
Iron	250
Lead	25
Magnesium	*
Manganese	50
Nickel	100
Potassium	*
Selenium	50(4)
Silver	50
Sodium	*
Thallium	50
Vanadium	100
Zinc	100
Mercury	0.5
Cyanide	100
Fluoride	400
NO_2/NO_3-N	200

(1) The levels shown indicate concentrations added in the final digestate of the spiked sample.

(2) The spike must be made with a solution containing antimony in the +5 oxidation state.

(3) The spike must be made with a solution containing arsenic in the +5 oxidation state.

(4) The spike must be made with a solution containing selenium in the +6 oxidation state.

*No spike required.

TABLE V
INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS
FOR ICP AND ICP/MS

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	720.0	720.0
Mo	10.0	10.0
Ti	10.0	10.0
As	0.0	0.100
Cd	0.0	0.050
Cr	0.0	0.100
Co	0.0	0.200
Cu	0.0	0.100
Mn	0.0	0.100
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.100
V	0.0	0.200
Zn	0.0	0.100

NOTE: See Exhibit D, Part E, for additional information.

TABLE VI
EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (mg/L)
ARISING FROM INTERFERENTS AT THE 100 mg/L LEVEL FOR ICP/OES

Analyte	Wavelength (nm)	Interferent Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE VII
TUNING SOLUTION FOR ICP/MS

The tuning solution must consist of the following elements at the stated concentrations.

Element	Concentration (ug/L)
^{7}Li	100
Co	100
In	100
Tl	100

TABLE VIII
TUNING, RESPONSE FACTOR AND MASS CALIBRATION CRITERIA
FOR ICP/MS

TUNING CRITERIA

m/z	Ion Abundance Criteria
7Li/59Co	(0.20 - 1.00)
59Co/59Co	(1.00)
115In/59Co	(0.75 - 2.00)
205Tl/59Co	(0.50 - 1.20)

RESPONSE FACTOR CRITERIA

m/z	Response Factor Criteria
7Li	(>2,000)
59Co	(>20,000)
115In	(>10,000)
102Ru	(<25)
205Tl	(> 1,000)

MASS CALIBRATION CRITERIA

m/z	Exact Mass
7Li	(6.9160 - 7.1160)
59Co	(58.8332 - 59.0332)
115In	(114.8040 - 115.0040)
205Tl	(204.8744 - 205.0744)

TABLE IX
MEMORY TEST SOLUTION FOR ICP/MS

The memory solution must consist of the following elements:*

Element	Concentration (mg/L)
Al	100
Ca	100
Fe	100
Mg	100
Na	100
K	100
C	200
Cl	720
Mo	10
P	100
S	100
Ti	10
Sb	10
As	10
Ba	10
Be	10
Cd	10
Cr	10
Co	10
Cu	10
Pb	10
Mn	10
Ni	10
Se	10
Ag	10
T	10
V	10
Zn	10

*Note: See Exhibit D Part E and Exhibit E for further references to the memory test solution.

TABLE X
INTERNAL STANDARDS THAT MAY BE USED IN ICP/MS

Internal Standard
Sc
Y
Rh
In
Tb
Ho
Bi
^{6}Li

TABLE XI
RECOMMENDED ELEMENTAL EXPRESSIONS FOR ISOBARIC INTERFERENCES
FOR ICP/MS

Element	Isobaric Correction	Expression Proportional to Elemental Concentration
Al	none	$(1.0000)(^{27}M)$
Sb	none	$(1.0000)(^{121}M)$
As	ArCl, Se	$(1.0000)(^{75}M)-(3.1278)(^{77}M)+(1.0177)(^{78}M)$
Ba	none	$(1.0000)(^{135}M)$
Be	none	$(1.0000)(^{9}M)$
Cd	MoO, Sn	$(1.0000)(^{114}M)-(0.0268)(^{118}M)-(1.6285)(^{108}M)$
Ca	none	$(1.0000)(^{44}M)$
Cr	none	$(1.0000)(^{52}M)$
Co	none	$(1.0000)(^{59}M)$
Cu	none	$(1.0000)(^{65}M)$
Fe	none	$(1.0000)(^{57}M)$
Pb	none	$(1.0000)(^{208}M)+(1.0000)(^{207}M)+(1.0000)(^{206}M)$
Mg	none	$(1.0000)(^{25}M)$
Mn	none	$(1.0000)(^{55}M)$
Ni	none	$(1.0000)(^{60}M)$
Ag	none	$(1.0000)(^{107}M)$
Tl	none	$(1.0000)(^{205}M)$
V	ClO, Cr	$(1.0000)(^{51}M)-(3.1081)(^{53}M)+(0.3524)(^{52}M)$
Zn	none	$(1.0000)(^{66}M)$
^{6}Li	Li(natural)	$(1.0000)(^{6}M)-(0.0813)(^{7}M)$
Sc	none	$(1.0000)(^{45}M)$
Y	none	$(1.0000)(^{89}M)$
Rh	none	$(1.0000)(^{103}M)$
In	Sn	$(1.0000)(^{115}M)-(0.0149)(^{118}M)$
Tb	none	$(1.0000)(^{159}M)$
Ho	none	$(1.0000)(^{165}M)$
Bi	none	$(1.0000)(^{209}M)$
Se	Ar_2	$(1.0000)(^{78}M)-(0.1869)(^{76}M)$

M = the total ion count rate at the specified mass.

TABLE XII

CONTRIBUTIONS OF CONCOMITANT ELEMENTS TO NEARBY ANALYTES FOR ICP/MS WHEN RESOLUTION AND MEASUREMENT SCHEMES VARY

Concentrations listed are the approximate level (mg/L) of interferent that gives an analyte concentration of 10 ug/L.

		Peak Width at 10% of the Peak Height			
		1.0 amu		0.8 amu	
	Interferent	Integration Width		Integration Width	
Analyte	Element	0.9 amu	0.3 amu	0.9 amu	0.3 amu
^{121}Sb	^{120}Sn	820	5	10	1
^{121}Sb	^{122}Te	77	none	1	none
^{75}As	^{74}Se, ^{76}Se	910	4	3	none
^{9}Be	^{10}B	1,200	12	9	1
^{112}Cd	^{113}In	1,700	8	10	none
^{114}Cd	^{115}In	>5,000	150	180	18
^{116}Cd	^{115}In	30	none	5	none
^{52}Cr	^{51}V	1.4	1.5	none	none
^{53}Cr	^{54}Fe	650	7	1	none
^{59}Co	^{58}Ni, ^{60}Ni	>1,500	6	2	none
^{63}Cu	^{62}Ni, ^{64}Ni	190	1	none	none
^{63}Cu	^{64}Zn	4,000	14	9	none
^{65}Cu	^{64}Ni	1	1	none	none
^{65}Cu	^{64}Zn, ^{66}Zn	>4,400	22	15	none
^{208}Pb	^{209}Bi	140	14	57	none
^{55}Mn	^{54}Fe, ^{56}Fe	900	8	4	none
^{58}Ni	^{59}Co	>3,000	96	75	7
^{60}Ni	^{59}Co	9	4	10	5
^{62}Ni	^{63}Cu	>8,500	690	4,500	16
^{107}Ag	^{106}Pd, ^{108}Pd	>2,400	22	80	4
^{107}Ag	^{106}Cd, ^{108}Cd	130	3	5	2
^{109}Ag	^{108}Pd, ^{110}Pd	1,800	12	36	3
^{109}Ag	^{108}Cd, ^{110}Cd	1,600	10	37	3
^{51}V	^{52}Cr	>2,100	45	410	1
^{64}Zn	^{65}Cu, ^{63}Cu	>7,800	57	410	2
^{66}Zn	^{65}Cu	2	none	3	2

TABLE XIII
ISOBARIC MOLECULAR-ION INTERFERENCES THAT COULD AFFECT THE ANALYTES

Analyte	Oxygen Inter.	Hydroxyl Inter.	Nitrogen Inter.	Chlorine Inter.	Sulfur Inter.	Carbon Inter.	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	SeCl, AsCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Co	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN			WC	
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++} Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}

TABLE XIII (cont'd)

Analyte	Oxygen Inter.	Hydroxyl Inter.	Nitrogen Inter.	Chlorine Inter.	Sulfur Inter.	Carbon Inter.	Other
^{61}Ni	ScO	CaOH	TiN	MgCl	SiS	TiC	Sn^{++}
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	FeOH	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo^{++}
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

Note: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

TABLE XIV
MASS CHOICES FOR ELEMENTS THAT MUST BE MONITORED
EITHER DURING THE ANALYTICAL RUN OR IN A SEPARATE SCAN FOR ICP/MS

Boldface and underlined masses indicate the masses that should have the most impact on data quality and the elemental equations used to collect the data. Underlined masses must be monitored.

Mass	Element of interest
27	**Aluminum**
121, 123	**Antimony**
75	**Arsenic**
138, 137, 136, **135**, 134, 132, 130	**Barium**
9	**Beryllium**
114, 112, 111, 110, 113, 116, 106, **108**	**Cadmium**
42, 43, **44**, 46, 48	**Calcium**
52, **53**, **50**, 54	**Chromium**
59	**Cobalt**
63, **65**	**Copper**
56, **54**, **57**, 58	**Iron**
208, **207**, **206**, 204	**Lead**
24, **25**, **26**	**Magnesium**
55	**Manganese**
202, **200**, 199, 201	**Mercury**
58, **60**, 62, **61**, 64	**Nickel**
39	**Potassium**
80, **78**, **82**, **76**, **77**, 74	**Selenium**
107, **109**	**Silver**
23	**Sodium**
205, 203	**Thallium**
51, **50**	**Vanadium**
64, **66**, **68**, **67**, 70	**Zinc**
83	**Krypton**
72	**Germanium**
139	**Lanthanum**
140	**Cerium**
129	**Xenon**
118	**Tin**
105	**Palladium**
47, **49**	**Titanium**
125	**Tellurium**
69	**Gallium**
35, 37	**Chlorine**
98, 96, 92, **97**, 94	**Molybdenum**

NOTE: Although the only masses that must be monitored are underlined, it is strongly recommended that the other elements be monitored to indicate other potential molecular interferences that could affect the data quality.

EXHIBIT D
ANALYTICAL METHODS

SECTION I
INTRODUCTION

The analytical method specified in Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limits (Exhibit C, Tables I and II). Analytical methods with higher detection limits may be used only if the sample concentration exceeds five times the documented detection limit of the instrument or method.

The sample for dissolved metal analysis will be filtered through a 0.450 membrane filter and preserved in the field before the samples are shipped to the laboratory. All instrument calibration standards must be matrix matched to the samples for dissolved metals. Matrix matching must be applied without affecting the original sample volume by more than ten percent.

All samples must initially be run undiluted (i.e., original sample or final product of sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range, re-analysis for that analyte(s) is required after appropriate dilution. The Contractor must use the lowest dilution factor necessary to bring each analyte within the valid analytical range (but not below the CRDL) and report the highest valid value for each analyte. Unless the Contractor can submit proof that dilution was required to attain valid results, both diluted and undiluted sample measurements must be contained in the raw data.

Labware must be acid cleaned according to EPA's manual "Methods for Chemical Analysis of Water and Wastes" or an equivalent procedure. Samples must be opened and digested in a hood. Stock solutions for standards may be purchased or made up as specified in Part A of Exhibit D. All sample dilutions shall be made with deionized water acidified to maintain constant acid strength.

Before water sample preparation is initiated, the Contractor must check the pH of all water samples, and note the pH in the sample preparation log.

Unless otherwise instructed by SMO, all samples must be mixed thoroughly prior to aliquoting for analysis or digestion.

Background corrections are required for all furnace AA measurements. Each furnace analysis requires at least two burns, except for full Method of Standard Additions (MSA).

All ICP, ICP-Hydride, and ICP/MS measurements shall require a minimum of two complete replicate exposures. Exposures for all samples and quality assurance measurements must be reported in the raw data in concentration units; intensities are not acceptable. The average of the exposures must be used for standardization, sample analysis, and in the reporting as specified in Exhibit B.

SECTION II
SAMPLE PRESERVATION AND HOLDING TIMES

A. PRESERVATION OF WATER SAMPLES

Measurement Parameter	Container(1)	Preservative(2)
Metals(3)	P,G	HNO_3 to pH <2
Cyanide, total and amenable to chlorination	P,G	0.6g ascorbic acid(4) NaOH to pH >12 Cool, maintain at 4°C(±2°C) until analysis
NO_2/NO_3-N	P,G	H_2SO_4 to pH <2
Fluoride	P,G	Cool, maintain at 4°C(± 2°C)

FOOTNOTES:

(1) Polyethylene (P) or glass (G).

(2) Sample preservation is performed by the sampler immediately upon sample collection.

(3) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved metals.

(4) Only used in the presence of residual chlorine.

B. HOLDING TIMES FOR WATER SAMPLES

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

Analyte	No. of Days Following Sample Receipt by Contractor
Mercury	26 days
Metals (other than mercury)	180 days
Cyanide	12 days
NO_2/NO_3-N	12 days
Fluoride	26 days

The Contractor must verify that the samples have been preserved properly using wide range pH paper. If the results of such verification do not conform to the requirements stated in A for preservation or in B for holding time, the Contractor must contact SMO for instructions before proceeding any further.

SECTION III
SAMPLE PREPARATION

Before collecting samples, a decision must be made by the data user as to the type of data desired, i.e., dissolved or total constituent analysis. This information will be included on the traffic report and the following preparation techniques shall be used for analysis under this contract.

All samples and standards (including QA/QC standards) must be matrix matched before analysis. Matrix matching must be applied without affecting the original sample volume by more than ten percent.

1. DISSOLVED METALS WATER SAMPLE PREPARATION

For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter and preserved in the field. This will be performed by the sampling team and recorded on the traffic report form. Analysis performed on a sample so treated shall be reported as "dissolved" concentrations.

2. TOTAL METALS WATER SAMPLE PREPARATION USING HOT PLATE DIGESTION

2.1 ACID DIGESTION PROCEDURE FOR FURNACE ATOMIC ABSORPTION ANALYSIS

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

Concentrations so determined shall be reported as "total".

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

2.2 ACID DIGESTION PROCEDURE FOR ICP, HYICP AND FLAME AA ANALYSES

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

Concentrations so determined shall be reported as "total".

2.3. ACID DIGESTION PROCEDURE FOR ICP/MS ANALYSIS

Shake the sample and transfer 100 mL of well-mixed sample to a 250 mL beaker, add 1.0 mL of (1+1) HNO_3 and 2 mL of 30% H_2O_2 to the sample. Cover with a watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C (temperature should be monitored with a thermometer) or until sample volume is reduced to between 25 and 50 mL, making certain that the sample does not boil. Cool the sample and filter to remove insoluble material. Adjust the sample volume to 100 mL with ASTM Type I water. The sample is now ready for analysis.

The sample preparation procedure for ICP-AES must be used for quantitation if this digestate contains more than 30 ug/L of silver, or more than 100 ug/L of antimony.

Concentrations so determined shall be reported as "total".

3. TOTAL METALS WATER SAMPLE PREPARATION USING MICROWAVE DIGESTION

3.1 SCOPE AND APPLICATION

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

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

*NOTE: All elements except for calcium, magnesium, potassium, and sodium may be analyzed by ICP/MS.

3.2 SUMMARY OF METHOD

3.2.1 A representative 45 mL water sample is digested in nitric acid. The digestate is then filtered to remove insoluble material. (NOTE: In place of filtering, the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material). If filtering is required, the sample is processed without volume correction since the final volume is identical to the initial volume in closed vessel digestions.

3.3 APPARATUS AND MATERIALS (MICROWAVE)

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

3.3.2 Microwave oven with programmable power settings up to at least 600 watts.

3.3.3 The system must use PFA Teflon^{R} digestion vessels (60 to 120 mL capacity) capable of withstanding pressures of up to 100 psi. Pressure venting vessels capable of controlled pressure relief at pressures exceeding 100 psi.

3.3.4 A double ported Teflon^{R} PFA overflow vessel (60 or 120 mL capacity).

3.3.5 A rotating table must be used to ensure homogeneous distribution of microwave radiation within the oven.

3.4 MICROWAVE CALIBRATION PROCEDURE

3.4.1 The calibration procedure is a critical step prior to the use of any microwave unit. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a single-point calibration at maximum power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple point calibration is necessary. If the unit power calibration needs multiple point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, and 50% power settings can be applied and the data plotted. The nonlinear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5 - 6.5 W and becomes the smallest unit of power that can be controlled. If 20 - 40 W are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

The following equation evaluates the power available for heating in a microwave cavity. This is accomplished by measuring the temperature rise in 1 Kg of water exposed to electromagnetic radiation for a fixed period amount of time.

Measurements are made on weighed replicates (5 replicates) of one kilogram samples of room temperature distilled water in thick-walled microwave transparent (Teflon®) vessels. The containers must be circulated continuously through the field for at least two (2) minutes at full power. The vessel(s) are removed from the microwave and stirred. After stirring, the temperature of the water is measured and recorded for use in the formula below. One kilogram of water, in one container or equally divided between two containers, is acceptable.

3.4.2 Calibration Formula - Weighed replicates (5) of 1 kilogram distilled room-temperature water in a microwave transparent vessel:

3.4.2.1 Measure initial temperature of water (T_i) to within 0.1°C. The starting temperature should be between 22 and 26°C.

3.4.2.2 Irradiate 1 Kilogram of water at full power, 100% (99, 98, 97, 95, 90, 80, 70, 60, or 50% power setting) for 120 seconds. The container must be circulated through the cavity at a rate of at least one revolution every 30 sec. during the irradiation.

3.4.2.3 Measure final temperature of water (T_f), after stirring, to within 0.1°C with stirring (an electronic stirrer using a large stir bar works best) within 30 sec of the end of microwave irradiation. Take the maximum reading.

3.4.2.4 Repeat for a new sample, for a total of 5 replicates per microwave setting, of distilled room-temperature water on a new clean container.

3.4.2.5 Calculate microwave power according to the formula:

$$\text{Power} = \frac{K \times Cp \times M \times T}{t}$$

$$(T_f - T_i) = T$$

$$\frac{K \times Cp \times 1000}{t} = 34.87$$

$$\text{Power} = 34.87 \times T$$

Where:

Power = The apparent power absorbed by the sample in watts. (W = joule-sec^{-2}).

K = The conversion factor for thermochemical calories-sec^{-1} to W (= 4.184).

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

M = The mass of the sample in grams (g).

T = $T_f - T_i$ in °C.

t = Time in seconds (s).

Derive an equation for the linear portion of the calibration range and determine the equivalent value in watts of the arbitrary setting scale. Use the actual power in watts to determine the appropriate setting of the particular microwave unit being used. Each microwave unit will have its own setting that corresponds to the actual power delivered to the samples.

3.4.3 Cleaning Procedure

3.4.3.1 The initial cleaning of the PFA vessels*:

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

3.4.3.1.2 Rinse in ASTM Type I water.

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

3.4.3.1.4 Rinse in ASTM Type I water.

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

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

*Note: All precautions must be taken to avoid preparation blank contamination.

3.5 CLEANING PROCEDURE BETWEEN SAMPLE DIGESTIONS

3.5.1 Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.

3.5.2 Rinse with 1:1 nitric acid.

3.5.3 Rinse three times with ASTM Type I water. If contaminants are found in the preparation blank, it is manadatory that steps 3.4.3.1.2 through 3.4.3.1.6 be strictly adhered to.

3.6 DIGESTION PROCEDURE FOR MICROWAVE

3.6.1 45 mL of the sample are measured into Teflon^{R} digestion vessels using volumetric glassware. 5 mL of high purity HNO_3 are added to the digestion vessels and the weight recorded to 0.02 g.

3.6.2 The caps with the pressure release valves are placed on the vessels hand tight and then tightened, using constant torque, to 12 ft.-lbs. Place 5 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the coracle may be done inside or outside the microwave. This procedure is energy balanced for five 45 mL water samples (each with 5 mL of acid) to produce consistent conditions and prevent alteration of the conditions. The initial temperature of the samples should be 24 $\pm$ 1°C. Blanks must have 45 mL of deionized water and the same amount of acid to be added to the microwave as a reagent blank.

3.6.3 Power Programming of Nitric Acid:

The 5 samples of 45 mL water and 5 mL nitric acid are irradiated for 10 minutes at 545 W and immediately cycled to the second program for 10 minutes at 344 W (BASED ON THE CALIBRATION OF THE MICROWAVE UNIT AS PREVIOUSLY DESCRIBED).

This program brings the samples to 160 $\pm$ 4°C in 10 minutes and then causes a slow rise in temperature between 165-170°C during the second 10 minutes.

3.6.4 Following the 20 minute program, the samples are left to cool in the microwave unit for 5 minutes, with the exhaust fan ON. The samples and/or carousel may then be removed from the microwave unit. Before opening the vessels, let cool until they are no longer hot to the touch.

3.6.5 After the sample vessel has cooled, weigh the sample vessel and compare to the initial weight as reported in the preparation log. Any sample vessel exhibiting a $\leq$ 0.5 g loss must have any excess sample from the associated collection vessel added to

the original sample vessel before proceeding with the sample preparation. Any sample vessel exhibiting a > 0.5 g loss must be identified in the preparation log and the sample redigested.

3.6.6 Sample Filtration:

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

4. DIGESTION PROCEDURE FOR MERCURY ANALYSIS

Because the digestion procedure for mercury is an integral part of the analysis system, it is discussed in Part F of the Sample Analysis Section (Section IV).

5. DISTILLATION PROCEDURE FOR CN ANALYSIS IN WATER

5.1 Place 500 mL of sample, or an aliquot diluted to 500 mL, in the 1 liter boiling flask. Add 50 mL of sodium hydroxide to the absorbing tube and dilute if necessary with ASTM Type I water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and tap in the train.

5.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

5.3 Slowly add 25 mL concentrated sulfuric acid through the air inlet tube. Rinse the tube with ASTM Type I water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution into the air inlet and wash down with a stream of water.

5.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

5.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with ASTM Type I water washings from the absorber tube.

5.6 The samples are now ready for analysis. The sample results must be corrected for by a factor of 2 in order to report final concentration based on an initial volume of 500 ml. If the initial volume is less than 500 mL, the sample must be diluted to 500 mL and an appropriate dilution factor must be indicated.

6. PREPARATION PROCEDURE FOR ION CHROMATOGRAPHY METHOD

Filtration of the sample and reagents is required. The sample matrix should be matched with all blanks, standards, and quality control samples to avoid inaccuracies resulting from possible standard curve deviation. The preparation procedure for the Ion Chromatography method is an integral part of the analysis system and is discussed in full in Part H of the Sample Analysis Section (Section IV).

7. PREPARATION PROCEDURE FOR AUTOMATED COLORIMETRIC METHODS

Filtration of the sample and reagents is required. The sample matrix should be matched with all blanks, standards, and quality control samples to avoid inaccuracies resulting from possible standard curve deviation. The preparation procedure for using Automated Colorimetric Methods is an integral part of the analysis system and is discussed in full in Part I of the Sample Analysis Section (Section IV).

8. PREPARATION PROCEDURE FOR ION SELECTIVE ELECTRODE METHOD

A pH 5 buffer containing a strong chelating agent must be added to all samples to eliminate interferences caused by pH and complexes forming. The preparation procedure for using the Ion Selective Electrode method is an integral part of the analysis system and is discussed in full in Part J of the Sample Analysis Section (Section IV).

SECTION IV
SAMPLE ANALYSIS

PART A - REAGENTS AND STANDARDS FOR METALS ANALYSIS AND SAMPLE PREPARATION

1. REAGENTS AND STANDARDS

1.1 Acids used in the preparation of standards and for sample processing must be below the CRDLs for the analytes of interest for the purpose of this method. Redistilled acids or ultra-pure acids are required for use with ICP/MS because of the high sensitivity of ICP/MS.

1.1.1 Acetic acid, conc. (sp gr 1.06)

1.1.2 Hydrochloric acid, conc. (sp gr 1.19)

1.1.3 Hydrochloric acid (1+1): Add 500 mL conc. HCl to 400 mL ASTM Type I water and dilute to 1 liter.

1.1.4 Nitric acid, conc. (sp gr 1.41)

1.1.5 Nitric acid (1+1): Add 500 mL conc. HNO_3 to 400 mL ASTM Type I water and dilute to 1 liter.

1.2 ASTM Type I Water (ASTM D1193) is required: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation for all reagents and calibration standards and as dilution water. Water must be monitored for analytes by the use of reagent blanks.

1.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105 °C, unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure element added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (mg/L)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (mg/L)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

NOTE: The recommended amounts of the starting materials specified for the following stock solutions are dependent upon the stoichiometry of the materials used as starting materials. Actual assay values of the starting materials should be used and the actual amounts corrected accordingly.

1.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolve 1.3903 g $Al(NO_3)_3 \cdot 9H_2O$ in 10 mL ASTM Type I water with 10 mL. HNO_3. Dilute to 1,000 mL with ASTM Type I water.

1.3.2 Antimony solution, stock, 1 mL = 100 ug Sb: Dissolve 0.1197 g Sb_2O_3 in 5 mL ASTM Type I water containing 0.1233 g $C_4O_6H_6$ (tartaric acid), add 500 mL ASTM Type I water, add 1 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

1.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g of As_2O_3 in 100 mL of ASTM Type I water containing 0.45 g NH_4OH. Acidify the solution with 12 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

1.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1437 g $BaCO_3$ in 10 mL ASTM Type I water with 10 mL conc. HNO_3. After dissolution is complete, warm the solution to degas. Dilute to 1,000 mL with ASTM Type I water.

1.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 4.5086 g $BeO(C_2H_3O_2)_6$ in ASTM Type I water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

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

1.3.7 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g $CaCO_3$ dried at 180 °C for 1 h before weighing in ASTM Type I water and dissolve cautiously with a minimum amount of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

1.3.8 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.2424 g of $(NH_4)_2Cr_2O_7$ in ASTM Type I water. Reduce the chromium with a few drops of hydrazine (NH_2NH_2), exhibited by the color change of the solution from orange to green. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

1.3.9 Cobalt solution, stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,00 mL with ASTM Type I water.

1.3.10 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1000 g Cu in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

1.3.11 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1000 g Fe in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

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

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

1.3.14 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.3149 g of manganese acetate Mn $(C_2H_3O_2)_2$ in ASTM Type I water. Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

1.3.15 Mercury solution, stock, 1 mL = 100 ug Hg: Dissolve 0.1708 g mercury (II) nitrate $Hg(NO_3)_2 \cdot (H_2O)$ in 75 mL of ASTM Type I water. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

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

1.3.17 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of ASTM Type 1 water and 10 mL conc. HNO_3. Dilute to 1000 mL with ASTM Type 1 water.

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

1.3.19 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2296 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

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

1.4 In the determination of trace elements, containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) depleting concentrations through adsorption. Thus the collection and treatment of the samples prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottles, whether borosilicate glass, linear polyethylene, or Teflon: detergent, Type II water, 1+1 hydrochloric acid, ASTM Type I water, 1+1 nitric acid, and Type I water.

Note: Chromic acid must not be used because chromium is one of the contract required analytes, and its use may lead to cross-contamination.

1.5 Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve, the preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure, and the rinse blank is used to flush the system between all samples and standards.

1.5.1 The calibration blank must be matrix matched to the standards.

1.5.2 The preparation blank must contain all the reagents in the same volumes as used in processing the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solutions used for analysis.

1.5.3 The rinse blank consists of the appropriate acid in ASTM Type I water. Prepare a sufficient quantity to flush the system between standards and samples.

1.6 The instrument check standard is the Initial and Continuing Calibration Verification solution (ICV and CCV) which is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration ranges. This solution must be prepared in the same acid matrix as the calibration standards.

1.7 The Interference Check Solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

1.7.1 Stock solutions for preparing ICS A and AB may be provided if available. Otherwise, refer to Exhibit C, Table V. They must be diluted tenfold (1+9) before use according to the instructions provided. The final ICS A and AB must be prepared weekly.

PART B
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD

1. SCOPE AND APPLICATION

1.1 Table I, in Exhibit C, lists elements along with the Contract Required Detection Limit for the analysis of metals in low concentration waters. Actual working detected limits are sample dependent and as the sample matrix varies, these concentrations may also vary. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account.

2. SUMMARY OF METHOD

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the line are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 3 should also be recognized and appropriate corrections made.

3. INTERFERENCES

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

3.1.1 Spectral interferences can be categorized as

3.1.1.1 Overlap of a spectral line from another element;

3.1.1.2 Unresolved overlap of molecular band spectra;

3.1.1.3 Background contribution from continuous or recombination phenomena; and

3.1.1.4 Background contribution from stray light from the line emission of high concentration elements.

The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

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

The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table VI, Exhibit C, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table VI, Exhibit C, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table VI, Exhibit C, indicate that measurable interferences were not observed from the interferent concentrations listed in Table V, Exhibit C. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table V, Exhibit C. At present, information on the listed

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

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

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

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

4. APPARATUS

4.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

4.1.1 Computer controlled atomic emission spectrometer with background correction.

4.1.2 Radio frequency generator.

4.1.3 Argon gas supply, welding grade or better.

4.2 Operational Requirements

4.2.1 System configuration -- 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 SET FORTH IN THIS METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

The data must include hardcopies or computer readable storage media which can be readily examined by an audit team. The data must demonstrate the presence or absence of all spectral interferences, including, but not limited to, the ones listed in Table VI of Exhibit C. The data must demonstrate defendable background correction points. This applies to simultaneous and sequential ICP instruments. Sequential ICP data must demonstrate the ability to select the correct peak from a spectrum in which nearby peaks from interferents are present.

5. REAGENTS AND STANDARDS (SEE PART A)

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 Mixed calibration standard solutions for ICP -- Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions, see PART A, in volumetric flasks. Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with ASTM Type I water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability.

Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

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

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

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

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

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

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

5.3 Two types of blanks are required for ICP analysis; the calibration blank is used in establishing the analytical curve while the preparation blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.3.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with ASTM Type I water. Prepare sufficient quantity to be used to flush the system between standards and samples.

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

5.4 The Interference Check Solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The ICS is prepared by the analyst, if not previously provided (Exhibit E). The ICS is used to verify that the interference levels are corrected by adequate background correction and within quality control limits.

6. PROCEDURE

6.1 Set up instrument with proper operating parameters established in Section 4.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

6.2 Initiate appropriate operating configuration of computer.

6.3 Calibration and Sample Analysis

6.3.1 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using matrix matched, mixed calibration standard solutions such as those described in

5.1. Calibrate the instrument for the analytes of interest using the calibration blank and at least a single standard. Flush the system with the calibration blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis. A minimum of two replicate exposures are required. The raw data must include the concentrations of elements in each integration as well as the average.

6.3.2 Begin the sample run flushing the system with the calibration blank solution between each sample.

6.3.3 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte.

7. **CALCULATIONS**

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

7.2 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

8. **QUALITY CONTROL**

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

8.3 The interference check solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

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PART C
HYDRIDE GENERATION INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD

1. SCOPE AND APPLICATION

1.1 This method covers the determination of antimony, arsenic and selenium in low concentration waters.

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. All sensitivities are somewhat compromised by this approach.

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 The efficiency with which the volatile hydrides of antimony, arsenic and selenium are generated is highly dependent on their oxidation states. The volatile hydrides of arsenic and antimony are most efficiently formed from +3 oxidation state while the volatile hydride of selenium is most efficiently generated from the +4 oxidation step. Aliquots of the sample 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 (IV) oxidation state to form a hydride.

2.2 In a continuous flow system, the samples 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 the different hydride formation reaction rates of the different oxidation states. The addition of the potassium iodide after the addition of the sodium borohydride eliminates the formation of elemental selenium by the iodide-iodine couple. It is the laboratory's responsibility to verify that optimum conditions for antimony, arsenic and selenium were obtained.

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 Spectrometer. The resulting free atoms are excited into higher electronic states. Atomic and ionic line emission spectra characteristic of the particular elements 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 elements 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.

3. **INTERFERENCES**

3.1 As discussed in Sections 2.1 and 2.2, proper adjustment of the oxidation states of the elements is important in obtaining accurate results.

3.2 Some of the transition elements, especially copper, cause suppression of the hydride formation by reacting to form insoluble salts. Selenium is affected more than the other elements 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 elements are eliminated because the interfering elements do not form hydrides and thus are not introduced into the plasma.

4. **APPARATUS**

4.1 Inductively Coupled Plasma-Atomic Emission Spectrometer

4.1.1 Computer-controlled inductively coupled argon plasma optical emission spectrometer system. NOTE: A fast sequential scanning instrument may be used if the Quality Control requirements set forth in this method can be met, although a simultaneous instrument is the instrument of choice.

4.1.2 Background correction capability.

4.1.3 Radiofrequency generator and coupling system.

4.1.4 Argon gas supply, welding grade or better.

4.1.5 Variable speed four channel peristaltic pump and pump tubing.

4.1.6 Hydride Manifold.

4.2 Operational Requirements

4.2.1 System Configuration -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst shall 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 SET FORTH IN THIS METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

The data must include hardcopies or computer readable storage media which can be readily examined by an audit team. The data must demonstrate defendable choices of instrument operating conditions which minimize interferences and optimize hydride generation.

5. **REAGENTS AND STANDARDS (SEE PART A)**

5.1 Fresh sodium borohydride solution (4.8% w/v in 0.25 N NaOH) must be prepared daily from ACS reagent grade chemicals. The sodium borohydride solution is essentially at saturation and will require stirring with a magnetic stirrer during the analysis.

5.2 Potassium iodide solution (8% w/v) is prepared from ACS reagent grade chemicals.

5.3 Calibration Standard Stock Solutions are prepared by dilution of the stock standard solutions (See Part A). The final solution must contain all three elements at the same concentration in 50% HCl. The standard stock solutions must consist of antimony, arsenic, and selenium in their lower oxidation states of plus five, plus five, and plus six respectively.

5.3.1 The concentration of the elements 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 the calibration of the instrument.

5.4 Three types of blanks are required for ICP-Hydride analysis. The calibration blank is used in establishing the calibration curve, the preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure, and the rinse blank is used to flush the system between all samples and standards.

5.4.1 The calibration blank solution and rinse blank both consist of 50% (v/v) HCl in ASTM Type I water. Note: As with all digested samples, add an equal volume of concentrated HCl to the blank to give a 50% (v/v) HCl analytical sample. This acid must be from the same lot of HCl as that used in preparation of the standards.

5.4.2 The preparation blank is prepared as specified in Exhibit E.

5.5 The continuing calibration verification standard final solution must contain all three elements at the same concentration in 50% (v/v) HCl.

5.6 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.

6. **PROCEDURE**

6.1 Set up the instrument with the proper operating parameters as established in Section 4.1. 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.

6.2 Initiate appropriate operating configuration of the computer.

6.3 Due to the diverse modifications of hydride manifolds, no detailed operational instructions can be provided. Instead, the analyst should consult the manufacturer instructions on which type of manifold would be best utilized with their particular instrument.

6.4 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 be checked and documented by continuously analyzing a blank solution after a high (greater than 10 mg/L) standard for each element.

6.5 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 Section E of this method. Direct monitoring of the photocurrent from the detector system for one of the elements 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 5 to 10 seconds during a cycle can establish the appropriate time intervals. Rinse times of at least 45 seconds are required between samples. It is required that the contractor document these parameters quarterly in the form of raw data results of this optimization. To test for sample carry-over, the analyst must analyze a high standard (greater than 10 mg/L) containing all the elements followed by the continuous aspiration for 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 element is the required wash time. If any sample solution analyzed contains any element 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.

6.6 The use of a mass flow controller on the carrier argon flow is recommended in place of a rotameter.

6.7 System Startup

6.7.1 All pump lines should be pumping only ASTM Type I water.

6.7.2 Place the sample pump line in the acid rinse solution. If potassium iodide is being used with the hydride manifold, place its sample line in the KI solution.

6.7.3 After the acid has entered the hydride manifold, 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 to help stabilize the plasma.

6.7.4 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 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. 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. CALIBRATION AND SAMPLE ANALYSIS

7.1 Calibrate the instrument using the appropriate matrix matched calibration standard solution(s). The calibration must include a calibration blank and at least one standard.

7.2 All standard, blank, and sample solutions must contain 50% (v/v) HCl. A change in the acid strength changes the slope of the calibration curve and can cause inaccurate results. All digested samples must be diluted 1:1 with concentrated HCl to give a 50% (v/v) HCl matrix in the analytical sample. The samples are then ready for analysis.

7.3 All standard, blank, and sample solutions must be heated at 90-100°C for a minimum of 10 minutes before being introduced into the hydride manifold. In order to ensure that sufficient heat is being applied, the results of two portions of the standards that were heated to a different extent (e.g., one for 10 minutes versus one for 15 minutes) must be compared. If the result yields a difference of more than 5%, the heating time must be increased until a difference of 5% or less is obtained. All standards, blanks, and sample solutions must be analyzed after being heated for the length of time that yields a 5% difference or less.

7.4 In order to determine if the sample result is to be calculated by the Method of Standard Addition (MSA), an analytical spike 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 Exhibit E. The spiking solution volume must not exceed 10% of the sample volume. The diluent should be 50% (v/v) HCl in the ASTM Type 1 water.

7.5 If MSA is required, follow the procedure given in Exhibit E.

7.6 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte.

8. CALCULATIONS

8.1 Calculate sample concentrations in (ug/L) by multiplying the analytical concentration by the appropriate dilution factors used.

8.2 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

9. QUALITY CONTROL

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

9.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

PART D
GRAPHITE FURNACE AND FLAME ATOMIC ABSORPTION SPECTROSCOPY METHOD

1. SCOPE AND APPLICATION

1.1 Graphite furnace atomic absorption procedures are provided to achieve the necessary sensitivity and detection limits needed for the analysis of drinking and ground/well water.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the various makes and models of satisfactory graphite furnace atomic absorption spectrophotometers.

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

2. SUMMARY OF METHOD

2.1 Using the furnace technique in conjunction with an atomic absorption spectrophotometer, 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 element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element 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 hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

3. INTERFERENCES

3.1 The composition of the sample matrix can have a major effect on the analysis. By modifying the sample matrix, 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. When the background interference cannot be compensated for, choose an alternate wavelength, chemically separate the analyte from the interferent, or use an alternate form of background correction, e.g., Zeeman 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 loss of analyte.

4. **APPARATUS**

4.1 Atomic absorption spectrophotometer. Single or dual channel, single or double beam instrument having a grating monochromator, 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 Operational Requirements

4.3.1 System configurations - - 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 on that particular instrument.

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 METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

The data must include hardcopies or computer readable storage media which can be readily examined by an audit team. The data must demonstrate defendable choices of furnace temperature program and matrix modifiers.

5. **REAGENTS AND STANDARDS (SEE PART A)**

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 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. Add 2 mL of (1+1) HNO_3 and dilute to 100 mL with ASTM Type I water. The calibration standards must be prepared using the same type of acid or combination of acids at the same concentration.

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 various acids used in the sample processing.

The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 to 100 mL with ASTM Type I water. The preparation blank is prepared as specified in Exhibit E.

6. PROCEDURE

6.1 Set up instrument with proper operating parameters established by the instrument manufacturer. The individual steps; drying, thermal pretreatment, and atomization require careful consideration to ensure each process is carried out effectively. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration. Background correction must be used.

6.2 Calibration and Sample Analysis

6.2.1 Calibrate instrument according to instrument manufacturer's recommended procedures, using calibration standard solutions. Beginning with the calibration blank and working towards the highest standard, run at least three standards and calibrate.

6.2.2 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 Exhibit E. The spiking solution volume must not exceed 10% of the sample volume.

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

6.4 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte.

7. CALCULATIONS

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

7.2 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

8. FLAME AA

8.1 Calcium (Method 215.1 CLP-M* Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-7 mg/L using a wavelength of 422.7 nm
Sensitivity: 0.08 mg/L
Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HCL. Dilute to 1000 mL with deionized distilled water. 1 mL = 0.5 mg Ca (500 mg/L).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 mL conc. HCl (Caution: Reaction is violent) and dilute to 500 mL with deionized distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 mL of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975]).
4. The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

*CLP-M modified for the Contract Laboratory Program.

8.2 Magnesium (Method 242.1 CLP-M* Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.02-0.5 mg/L using a wavelength of 285.2 nm
Sensitivity: 0.007 mg/L
Detection Limit: 0.001 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 mL of redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 0.50 mg Mg (500 mg/L).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with deionized distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/L.
2. The following line may also be used: 202.5 nm Relative Sensitivity 25.
3. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

8.3 Potassium (Method 258.1 CLP-M* Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-2 mg/L using a wavelength of 766.5 nm
Sensitivity: 0.04 mg/L
Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 mL = 0.10 mg K (100 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in the buffer zone.
2. The 404.4 nm line may also be used. This line has a relative sensitivity of 500.
3. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

8.4 Sodium (Method 273.1 CLP-M* Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.03-1 mg/L using a wavelength of 589.6 nm
Sensitivity: 0.015 mg/L
Detection Limit: 0.002 mg/L

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 mL = 1 mg Na (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

9. QUALITY CONTROL

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

9.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

*CLP-M modified for the Contract Laboratory Program.

PART E
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 Metals for which this method is applicable are listed in Table II, Exhibit C in low concentration water samples. Instrument detection limits, sensitivities, and linear ranges for these elements will vary with the matrices, instrumentation, and operating conditions. Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and the correction of spectral, chemical, and physical interferences in ICP-MS. Experience requirement is 1 year on a commercially available ICP-MS.

2. SUMMARY OF METHOD

2.1 The method describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and by means of a water cooled interface, introduced into a quadrupole mass spectrometer, capable of providing a resolution better than or equal to 1 amu peak width at 10% of the peak height. The water-cooled interface consisting of tandem skimmers, is differentially pumped and leads into the high vacuum chamber of the mass spectrometer. The ions and ion clusters produced in the plasma and those formed during the introduction of the ion beam into the mass spectrometer, are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Table XIII, Exhibit C, shows isobaric interferences and the secondary masses which would be analyzed to correct for these interferences. A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting out the appropriate signal from the isotope of interest. Data that is corrected must be noted in the report along with the exact calculations used. Commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, and very high ion currents at adjacent masses can contribute to ion signals at the mass of interest. Table XII, Exhibit C, shows approximate concentrations at which adjacent masses give rise to a contribution of 10 ug/L to the analyte of interest at a resolution of 1 amu at 10% peak height, if the mass were chosen for quantitation. It should be noted that the information described in Table XII, Exhibit C, was experimentally derived and the interferences which are described

occur from several different sources. One interference is the effect of resolution on adjacent peaks. This has a larger effect at 1 amu less than the interferent than at 1 amu greater than the interferent's mass due to the trapezoidal peak shape associated with a quadrupole mass spectrometer. Another interference which would be observed is the formation of a hydride ion. These interferences only cause an interference at 1 amu greater than the interferent's mass. It should also be remembered that these interferences are not necessarily linear and attempts should not be made to extrapolate the values to a particular data set. The table has been included for its informational content alone.

3.2 Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge. Table XIII, Exhibit C, lists isobaric molecular-ion interferences which could affect the analytes. It should be noted that many of these interferences are extremely rare, but adverse effects on data quality could occur if the individual constituents occurred in the sample at sufficiently high concentrations. When the interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections to the data must be applied. Corrections for molecular-ion interferences may either be based upon the natural isotope ratios of the molecular ion or a determination of the actual amount of interference which occurs when the interferant is present.

If a correction for an oxide ion is used, the correction may be normalized to the extent of oxide formation of an appropriate internal standard previously demonstrated to form the same level of oxide as the interferant. This second type of correction has been reported for oxide ion corrections using ThO/Th for use on rare earth elements. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature.

3.3 Physical interferences are effects associated with the sample nebulization and transport processes as well as ion-transmission efficiencies. Nebulization and transport processes are those in which the matrix component causes a change in surface tension or viscosity in a manner different from the standards used in performing calibration. Internal standards have been used to correct for these interferences. The interferences are primarily suppressions and are seen by the lighter elements more than the heavier elements. The effects are greater for matrix components with heavier atomic mass than for matrix components with lighter atomic mass. Changes in matrix composition therefore can cause significant suppressions and enhancements. Dissolved-solid levels can contribute deposits on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 ppm) have been recommended to minimize solid deposition. Internal standards must be affected to the same degree as the analyte to demonstrate that they compensate for these interferences. A minimum of three internal standards, listed in Table X Exhibit C, bracketing the mass range, must be used. When the intensity level of an internal standard is less than 30% or greater than 125% of the intensity of the first standard used during calibration, the sample must be reanalyzed

after performing a fivefold (1+4) dilution. The intensity levels of the internal standards for the Continuing Calibration Blank and Continuing Calibration Verification Solution must agree within ±20 percent of the intensity level of the internal standard of the Initial calibration blank solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples at no additional cost.

3.4 Memory interferences are effects which are dependant upon the relative concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer used, affect the extent of the memory interferences which are present. To verify that memory effects do not have an adverse impact on data quality, the memory test must be performed on the tuned and calibrated instrument before any analyses are performed. A multielement memory test solution containing levels of analytes as specified in Table IX, Exhibit C, is aspirated into the system for a normal sample exposure period. A blank solution is then introduced, noting the time when the uptake tube is switched to the blank solution. After the normal routine rinse time has elapsed, begin a routine analysis of the blank solution. Inspect the resulting data to see if any analytes are in excess of the IDL. If there are, reanalyze the blank to eliminate the possibility of actual blank contamination. A decreased value on the second analysis indicates a memory problem rather than blank contamination. If a memory problem does exist (see Exhibit E) for a given analyte, increase the rinse time until the system passes the memory test. If the increased rinse time is not feasible from a sample throughput standpoint, a hardware change may be necessary.

4. APPARATUS AND MATERIALS

4.1 Inductively coupled plasma - mass spectrometer:

4.1.1 System capable of 1 amu resolution from 6-253 amu with a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%)

4.2 Operational Requirements

4.2.1 System Configuration -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instruction can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limits (IDL's), precision, linear dynamic range and interference effects must be established for each analyte on a particular instrument. All reported

measurements must be within the instrumental linear ranges. The analyst must maintain quality control data confirming instrument performance and analytical results.

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 METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

The data must include hardcopies and computer readable storage media which can be readily examined by an audit team. The data must demonstrate defendable choices of instrument operating conditions which minimize interferences such as oxides.

4.3 Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing which invalidates the calibration curve, causes instability, and invalidates sample analyses. Samples run during such periods are required reruns at no additional cost.

4.4 Sensitivity, Instrument Detection Limits (IDL's), precision, linear dynamic range, and interference effects must be established for each analyte on a particular instrument. These parameters must be determined for each configuration used if an instrument is equipped with dual detector hardware. All reported measurements must be within the instrumental linear dynamic ranges. All reported measurements from a less sensitive detector configuration must exceed five times the documented instrumental detection limit for that detector configuration. The analyst must maintain quality control data confirming instrument performance and analytical results.

5. REAGENTS AND STANDARDS (SEE PART A)

5.1 Acids used in the preparation of standards and for sample processing must be below the IDL's for the analytes of interest for the purpose of a study. Redistilled acids or ultra-pure acids are required for use with ICP-MS because of the high sensitivity of ICP-MS. Nitric acid at less than 2 percent (v/v) is preferred for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used, as demonstrated in Table XIII, Exhibit C. Concentrations of antimony and silver above 300 ug/L require 1% (v/v) HCl for stability.

5.2 Internal standards must be used to monitor and correct for changes that occur from differences between standards and samples. This information must be clearly reported in the raw data. The changes for which internal standards correct are primarily physical interferences. Internal standards must be present in all standards and samples at identical levels by mixing the internal standard to the solution being

nebulized prior to the nebulizer. This may be accomplished by using a second channel of the peristaltic pump to add the internal standard to the uptake tube. If adding the solution to the uptake tube is not used then the internal standard must be added in two separate aliquots to the samples and standards to prevent the possibility of improperly spiking the internal standard levels. The double spiking ensures that misquantitation will not occur based upon a single internal standard spike. Double spiking may occur either by adding a constant volume of internal standard concentrate to identical volumes of the standards and prepared samples, or by diluting the internal standard to the appropriate level for its use in the analyses. One typical example is to measure out 10.0 mL of all standards and samples into individual containers, then 0.100 mL of a 10 mg/L solution of the internal standard is added to each of the containers. This adds identical amounts of the internal standard to each solution for analysis. The concentrations of the analyte levels in the standards do not have to be corrected for the dilution which occurs because the dilution is canceled out when corrections to the samples are made for their dilution.

5.2.1 Bismuth internal standard solution, stock, 1 mL = 100 ug Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

5.2.2 Holmium internal standard solution, stock, 1 mL = 100 ug Ho: Dissolve 0.1757 g $Ho_2(CO_3)_2 \cdot 5H_2O$) in 10 mL ASTM Type I water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

5.2.3 Indium internal standard solution, stock, 1 mL = 100 ug In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with ASTM Type I water.

5.2.4 Lithium internal standard solution, stock, 1 mL = 100 ug ^{6} Li: Dissolve 0.6312 g 95 atom % enriched ^6Li, Li_2CO_3 in 10 ml of ASTM Type I water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

5.2.5 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in ASTM Type I water. Dilute to 1,000 mL with ASTM Type I water.

5.2.6 Rhodium internal standard solution, stock, 1 mL = 100 ug Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL ASTM Type I water. Add 100 mL conc. HCl and dilute to 1,000 mL with ASTM Type I water.

5.2.7 Scandium internal standard solution, stock, 1 mL = 100 ug Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 ml conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

5.2.8 Titanium solution, stock, 1 mL = 100 ug Ti: Dissolve 0.4133 g $(NH_4)_2TiF_6$ in ASTM Type I water. Add 2 drops of conc. HF and dilute to 1,000 mL with ASTM Type I water.

5.2.9 Terbium internal standard solution, stock, 1 mL = 100 ug Tb: Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 ml conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

5.2.10 Yttrium internal standard solution, stock, 1 mL = 100 ug Y: Dissolve 0.2316 g $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL (1+1) HNO_3. Add 5 ml conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

5.3 Mixed calibration standard solutions -- Dilute the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in ASTM Type I water along with the selected concentration of internal standards such that there is an appropriate internal standard element for each of the analytes (see Table X, Exhibit C). Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned not previously used FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability. Although not specifically required, some typical calibration standard combinations follow.

5.3.1 Mixed standard solution I -- Manganese, beryllium, cadmium, lead, silver, barium, copper, cobalt, nickel and zinc.

5.3.2 Mixed standard solution II - Arsenic, chromium, thallium, and aluminum.

5.3.3 Mixed standard solution III -- Antimony, vanadium, iron.

5.3.4 Mixed standard solution IV -- Bismuth, holmium, indium, scandium, yttrium, and terbium.

5.3.5 Mixed standard solution V -- Rhodium.

Note: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of ASTM Type I water and warm the flask until the solution clears. Cool and dilute to 100 mL with ASTM Type I water. For this acid combination the silver concentration must be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days.

5.4 Three types of blanks are required for the analysis. The calibration blank is used in establishing and monitoring the calibration curve, the preparation blank is used to monitor for (SO, ICB, CCB) possible contamination resulting from the sample preparation procedure, and the rinse blank is used to flush the system between all samples and standards.

5.4.1 The calibration blank consists of 1 percent HNO_3 (v/v) in ASTM Type I water along with the selected concentration of internal standards such that there is an appropriate internal standard element for each of the analytes (see Table X, Exhibit C).

5.4.2 The preparation blank must contain all the reagents in the same volumes as used in processing the samples. The preparation blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solutions used for analysis (see Exhibit E).

5.4.3 The rinse blank consists of 2 percent HNO_3 (v/v) in ASTM Type I water. Prepare a sufficient quantity to flush the system between standards and samples.

5.5 The Interference Check Solution(S) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The ICS solution is detailed in Table V, Exhibit C. The chloride concentration provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Since the natural abundance of ^{35}Cl at 75.8 percent is 3.13 times the ^{37}Cl abundance of 24.2 percent, the ion corrections can be calculated with adjustments for isobaric contributions. Iron is used to demonstrate adequate resolution of the spectrometer on manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement scheme to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.5.1 Stock solutions for preparing ICS solutions A and AB may be provided if available. Otherwise, refer to Table V, Exhibit C. They must be diluted before use according to the instruction provided. The prepared ICS solutions A and AB must be prepared weekly.

5.5.2 Mixed ICS solution I may be prepared by adding 13.903 g $Al(NO_3)_3.9H_2O$, 2.498 g $CaCO_3$ dried at 180°C for 1 h before weighing, 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3, and 1.767 g K_2CO_3 to 25 mL of ASTM Type I water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with ASTM Type I water.

5.5.3 Mixed ICS solution II may be prepared by slowly adding 7.44 g 85% H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g critic acid $C_6O_7H_8$ to 100 mL of ASTM Type I water. Dilute to 1,000 mL with ASTM Type I water.

5.5.4 Mixed ICS solution III may be prepared by adding 5 mL each of arsenic stock solution, chromium stock solution, copper stock solution, and zinc stock solution, 10 mL each of cobalt stock solution, nickel stock solution, and vanadium stock solution, and 2.5 mL of cadmium stock solution. Dilute to 100 mL with 2% HNO_3.

5.5.5 ICS A may be prepared by adding 10 mL of mixed ICS solution I, 10 mL each of titanium stock solution, and molybdenum stock solution, and 5 mL of mixed ICS solution II. Dilute to 100 mL with ASTM Type I water. ICS solution A must be prepared fresh weekly.

5.5.6 ICS AB may be prepared by adding 10 mL of mixed ICS solution I, 10 mL each of titanium stock solution and molybdenum stock solution, 5 mL of mixed ICS solution II, and 2 mL of mixed ICS solution III. Dilute to 100 mL with ASTM Type I water. ICS solution AB must be prepared fresh weekly.

6. PROCEDURE

6.1 Initiate appropriate operating configuration of instrument computer.

6.2 Set up the instrument with the proper operating parameters. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by running the tuning solution (Table VII, Exhibit C) at least four times with relative standard deviations of less than 10% for the analytes contained in the tuning solution.

6.3 Conduct mass calibration and resolution checks using the tuning solution (100 ppb of the elements Li, Co, In, and Tl). The intensities on the forms in Exhibit B (see Table VIII in Exhibit C) for the response factor criteria are recommendations which might be helpful when setting up the instruments but are not required criteria. The mass calibration must meet the criteria specified in Table VIII, Exhibit C, if mass calibration exceed those criteria then the mass calibration must be adjusted to the correct values. The resolution must also be verified to be less than 1.0 amu full width at 10 percent peak height. To verify, the tuning solution must be analyzed at the beginning and end of each 8 hour shift, and pass the tuning criteria.

6.4 Calibration and Sample Analysis

6.4.1 Calibrate the instrument for the analytes of interest using the calibration blank and at least a single standard according to the manufacturer's recommended procedure for each detector configuration which will be used in analysis. Flush the system with the rinse blank between each standard solution. Report each integration during the calibration and sample analysis and

use the average of the multiple integrations for both standardization and sample analysis. A minimum of two replicate integrations are required for both calibration and sample analysis. The raw data must include the concentrations of elements in each integration as well as the average. Additionally, if different detector configurations are used, the raw data must indicate which detector configuration is being used.

NOTE: Some elements (such as Hg, W, and Mo) require extended flushing times which need to be determined for each instrumental system. Run Memory Test on solution in Table IX, Exhibit C, to verify that memory problems will not affect the data quality.

6.5 As a minimum, all masses which would affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. This information is to be used to assess data quality and as a minimum must include the masses which are boldfaced and underlined, listed in Table XIV, Exhibit C, for each element. These masses must be monitored simultaneously in a separate scan or at the time quantification occurs.

6.6 Flush the system with the rinse blank solution for a least 30 seconds before the analysis of each sample. Aspirate each sample for at least 30 seconds before collecting data.

6.7 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte.

7. CALCULATIONS

7.1 If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.2 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples. No other units are acceptable.

8. QUALITY CONTROL

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

8.3 To obtain analyte data of known quality, it is necessary to measure for more than the analytes of interest in order to know the required interference corrections. If the concentrations of interference sources (such a C, Cl, Mo, Zr, W) are below the levels that show an effect on the analyte level, uncorrected equations may be used provided all QA criteria are met. It should be noted that monitoring the interference sources does not necessarily require monitoring the

interference itself, but that a molecular species may be monitored to indicate the presence of the interference. When corrected equations are used all QA criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions which could impact the analytes of interest. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance. These tests will enable the analyst to detect positive or negative interferences that distort the accuracy of the reported values.

8.4 The interference check solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The ICS is used to verify that the interference levels are corrected by the data system within QC limits.

9. REFERENCES

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PART F
MERCURY ANALYSIS IN WATER

1. SCOPE AND APPLICATION

1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

1.2 The range of the method may be varied through instrument and/or recorder expansion and sample size. Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved.

2. SUMMARY OF METHOD

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. INTERFERENCES

3.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water .

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.4 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility.

4. APPARATUS

4.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

IT IS THE RESPONSIBILITY OF THE ANALYST TO VERIFY THAT THE INSTRUMENT CONFIGURATION AND OPERATION CONDITIONS USED SATISFY THE ANALYTICAL REQUIREMENTS SET FORTH IN THIS METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

4.2 Mercury Hollow Cathode Lamp: Argon filled, or equivalent.

4.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used.

4.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

4.7 Aeration Tubing: A straight glass fit having a coarse porosity. Tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate. In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

4.9 Autoanalyzer system (for automated spectrometric method) including:

4.9.1 Sampler with provisions for sample mixing.

4.9.2 Proportioning pump.

4.9.3 Mercury manifold.

4.9.4 High temperature heating bath with two distillation coils.

4.9.5 Vapor-liquid separator

5. REAGENTS AND STANDARDS (SEE PART A)

5.1 Sulfuric Acid, Conc: Reagent grade.

5.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL conc. sulfuric acid to 1.0 liter with ASTM Type I water.

5.1.2 Sulfuric acid, 2 N: Dilute 56 mL of conc. sulfuric acid to 1 liter with ASTM Type I water.

5.1.3 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with ASTM Type I water.

5.2 Nitric Acid, Conc: Reagent grade of low mercury content.

5.2.1. Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of concentrated nitric acid to 1 liter with ASTM Type I water.

5.3 Stannous Sulfate (Stannous chloride may be used in place of stannous sulfate.)

5.3.1 Manual method: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

5.3.2 Automated method: Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

5.4 Sodium Chloride-Hyroxylamine Sulfate Solution (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.4.1 Manual method: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in ASTM Type I water and dilute to 100 mL.

5.4.2 Automated method: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in ASTM Type I water to 1 liter.

5.5 Potassium Permanganate

5.5.1 Manual method: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of ASTM Type I water.

5.5.2 Automated method:

5.5.2.1 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of ASTM Type I water.

5.5.2.2 0.1 N. Dissolve 3.16 g of potassium permanganate in ASTM Type I water and dilute to 1 liter.

5.6 Potassium Persulfate

5.6.1 Manual method: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of ASTM Type I water.

5.6.2 Automated method: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of ASTM Type I water.

5.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

5.8 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate and 10% sulfuric acid.

6. PROCEDURE

6.1 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.

6.2 Manual Spectrometric Determination

6.2.1 Calibration and Sample Analysis

6.2.1.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough ASTM Type I water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of conc. sulfuric acid and 2.5 mL of conc. nitric acid to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 lbs. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the

aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4, or b) 0.25% iodine in a 3% a KI solution. A specially treated charcoal that will adsorb mercury vapor is available.

6.2.2. Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of sulfuric acid and 2.5 mL of conc. nitric acid mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle (see Note 6). Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate (see Note 7). Purge the head space in the BOD bottle for at least 1 minute and add 5 mL of Stannous Sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until KMnO4 is completely reduced.

6.3 Automated Spectrometric Determination

6.3.1 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.

6.3.2 Calibration and Sample Analysis

6.3.2.1 From the Working Mercury solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/L.

6.3.2.2 Set up manifold.

6.3.2.3 Feeding all the reagents through the system with acid wash solution through the sample line, adjust heating bath to 105°C. Pump reagents through the system until a steady baseline is obtained.

6.3.2.4 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

6.3.2.5 Arrange working mercury standards from 0.0 to 20.0 ug Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.

6.3.2.6 Prepare standard curve by plotting peak height of processed standards against concentration values.

6.3.2 Determine concentration of samples by comparing sample peak height with standard curve.

6.3.3 After the analysis is complete put all lines except the sulfuric acid line in distilled water to wash out system. After flushing, wash out the sulfuric acid line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

7. CALCULATIONS

7.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/L} = \text{ug Hg in aliquot} \times \frac{1{,}000}{\text{volume of aliquot in mL}}$$

7.3 Report mercury concentrations as follows: Below 0.20 ug/L, 0.20 ug between 0.20 and 10.0 ug/L, two significant figures; equal to or above 10.0 ug/L, three significant figures.

7.4 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

7.5 If dilutions were performed, the appropriate corrections must be applied to the sample values.

8. QUALITY CONTROL

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

9. REFERENCES

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7. Standard Methods for the Examination of Water and Wastewater

PART G
METHOD FOR TOTAL CYANIDE ANALYSIS IN WATER

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of cyanide in low concentration water samples.

1.2 The manual colorometric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 10 ug/L.

1.3 The working range of the semi-automated spectrophotometric method is 5 to 200 ug/L. Higher level samples must be diluted to fall within the working range.

2. SUMMARY OF METHOD

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridinebarbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3. INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 6.1.

3.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

3.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the

condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

4. APPARATUS

4.1 Reflux distillation apparatus. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

4.2 Microburet, 5.0 mL (for titration)

4.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).

4.4 For automated spectrophotometric method:

4.4.1 Sampler

4.4.2 Pump

4.4.3 Cyanide Manifold

4.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters

4.4.5 Recorder

4.4.6 Data System (optional)

4.4.7 Glass or plastic tubes for the sampler

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 Distillation and Preparation Reagents

5.2.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in ASTM Type I water, and dilute to 1 liter with distilled water.

5.2.2 Cadmium carbonate: powdered

5.2.3 Ascorbic acid: crystals

5.2.4 Sulfuric acid: concentrated

5.2.5 Magnesium chloride solution: Weight 510 g of $MgCl_2.6H_2O$ into a 1000 mL flask, dissolved and dilute to 1 liter with ASTM Type I water.

5.3 Stock Standards and Titration Reagents

5.3.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of ASTM Type I water. Standardize with 0.0192 N $AgNO_3$.

5.3.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with ASTM Type I water.

5.3.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with ASTM Type I water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).

5.3.4 Sodium hydroxide solution, 0.25 N: Dissolve 10 g or NaOH in ASTM Type I water and dilute to 1 liter.

5.4 Manual Spectrophotometric Reagents

5.4.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4.H2O$ in a liter of ASTM Type I water. Refrigerate this solution.

5.4.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of ASTM Type I water and refrigerate until ready to use. Prepare fresh weekly.

5.4.3 Color Reagent-One of the following may be used:

5.4.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough ASTM Type I water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with ASTM Type I water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

5.4.3.2 Pyridine-pyrazolin-5-one solution:

5.4.3.2.1 3-Methyl-1phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of ASTM Tpye I water, heat to 60°C with stirring. Cool to room temperature.

5.4.3.2.2 3,3'Dimethyl-1,1'-diphenyl [4,4'-bi-2 pyrazolin]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

5.4.3.2.3 Pour solution (5.4.3.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter

paper pour solution (5.4.3.2.2) collecting the filtrate in the same container as filtrate from (5.4.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

5.5 Semi-Automated Spectrophotometric Reagents

5.5.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in ASTM Type I water and dilute to 100 mL. Prepare fresh daily.

5.5.2 Phosphate buffer: Dissolve 138 g of $NaH_2PO_4.H_2O$ in ASTM Type I water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C(±2°C).

5.5.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of ASTM Type I water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. Dilute to about 900 mL with ASTM Type I water and mix until the barbituric acid is dissolved. Dilute to 1 liter with ASTM Type I water. Store at 4°C(±2°C).

5.5.4 Sampler wash: Dissolve 10 g of NaOH in ASTM Type I water and dilute to 1 liter.

6. PROCEDURE

6.1 Manual Spectrophotometric Determination (Option B)

6.1.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution. Add 15.0 mL of sodium phosphate solution and mix.

6.1.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix. Dilute to mark with ASTM Type I water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

6.1.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution and mix. Dilute to mark with ASTM Type I water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm

cell. NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

6.1.2 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Detection Limit (CRDL). To each standard, add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with ASTM Type I water. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution. As an example, standard solutions could be prepared as follows:

mL of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 mL
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	75
20.0	100

6.1.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not agree within ±15% of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding.

6.1.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL).

6.2 Semi-Automated Spectrophotometric Determination (Option C)

6.2.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

6.2.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

mL Standard Solution diluted to 1 liter	Concentration ug CN/L
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C)

6.2.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

6.2.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

7. CALCULATIONS

7.1 If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 mL and the distillate volume was 250 mL). Also, correct for any dilutions which were made before or after distillation.

7.2 If the colorimetric procedure is used, calculate the cyanide, in ug/L, in the original sample as follows:

$$\text{CN, ug/L} = \frac{A \times 1{,}000 \text{ mL/L}}{B} \times \frac{50 \text{ mL}}{C}$$

Where: A = ug CN read from standard curve (per 250 mL
B = mL of original sample for distillation
C = mL taken for colorimetric analysis
50 mL = volume of original sample aliquot
1,000 mL = conversion mL to L

7.3 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples. NO other units are acceptable.

7.4 If dilutions were performed, the appropriate corrections must be applied to the sample values.

8. QUALITY CONTROL

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

9. REFERENCES

9.1 Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.

9.2 Methods for "Chemical Analysis of Water and Wastes", March 1979, EPA publication #600/4-79-02.

9.3 Op. cit. (#4), Methods 335.2.

9.4 "Operation RN Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.

9.5 "Users Guide for the Continuous Flow Analyzer Automation System", EMSL U.S. EPA, Cincinnati, OH (1981).

PART H
ION CHROMATOGRAPHY METHOD FOR NO_2/NO_3-N

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of NO_2/NO_3-N in low concentration water samples.

1.2 The range of the method may be varied through instrument and/or sample size. Using a 100 uL sample size, a detection limit of 10 ug/L for NO_2/NO_3-N can be achieved.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram.

2. SUMMARY OF METHOD

2.1 A small volume of sample, typically 0.1 - 1.0 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressor column, and conductivity detector.

3. INTERFERENCES

3.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. If it is determined that this type of interference cannot be resolved, NO_2/NO_3-N must be determined by using the colorimetric method specified in Part I.

3.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

3.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

3.4 The use of concentrated sulfuric acid, in the preservation of the sample, can cause possible instrument interference problems in the analysis of the target analyte. The analyst should be aware of the type of preservative used and take the appropriate action, if necessary. Sulfuric acid must be neutralized before proceeding with the analysis.

4. APPARATUS

4.1 Ion chromatograph: Any analytical system complete with ion chromatograph and all required accessories including analytical columns, detector, stripchart recorder and a data system for peak integration.

4.1.1 Anion guard column: 4 x 50mm.

4.1.2 Anion separator column: 4 x 250mm.

4.1.3 Anion suppressor column: fiber, or equivalent.

4.1.4 Detector: Conductivity cell, approximately 6 ul volume.

4.2 Operational Requirements

4.2.1 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. Other columns, chromatographic conditions, or detectors may be used if the QA requirements in Exhibit E are met. Sensitivity, instrumental detection limits, precision, retention time and other column chromatographic conditions must be investigated and established for NO_2/NO_3-N on that particular instrument.

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 METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

The data must include hardcopies or computer readable storage media which can be readily examined by an audit team. The data must demonstrate defendable choices of instrument operating conditions which minimize interferences such as sulfide co-elution.

5. REAGENTS AND STANDARDS

5.1 Reagent water: ASTM Type I water, free of anions of interest and containing no particles larger than 0.20 microns.

5.2 Eluent solution: Sodium bicarbonate 0.003 M, sodium carbonate 0.0024 M. Dissolve 1.0081 g sodium bicarbonate ($NaHCO_3$) and 1.0176 g of sodium carbonate (Na_2CO_3) in reagent water and dilute to 4 liters.

5.2.1 Eluent spiking solution: sodium bicarbonate 0.030 M, sodium carbonate 0.0240 M. Dissolve 2.5203 g sodium bicarbonate ($NaHCO_3$) and 2.5440 g of sodium carbonate (NA_2CO_3) in reagent water and dilute to 1 liter.

5.3 Regeneration solution (fiber suppressor, or equivalent): Sulfuric acid 0.025 N. Dilute 8 mL conc. sulfuric acid (H_2SO_4) to 4 liters with reagent water.

5.4 Stock standards, 1000 mg/L: Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 minutes) as listed below.

5.4.1 NO_2/NO_3-N 1000 mg/L: dissolve 6.0679 g of sodium nitrate ($NaNO_3$) and 4.9257 g sodium nitrite ($NaNO_2$) in reagent water and dilute to 1 liter.

6. PROCEDURE

6.1 Establish a stable baseline with working eluent running through the system and establish ion chromatographic operating parameters equivalent to obtain the CRDL's. This requires at least 30 minutes.

6.2 Calibration and Sample Analysis

6.2.1 Matrix matching, with the samples, is mandatory for all blanks, standards, and quality to control samples to avoid inaccurate concentration values due to possible standard curve deviation.

6.2.2 For NO_2/NO_3-N, prepare a combined calibration standard at a minimum of three concentration levels and a blank by adding accurately measured volumes of the stock standards to a volumetric flask and diluting to volume with reagent water. One of the standards must be at the CRDL. The attenuator range settings must be linear.

6.2.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

6.2.4 The working calibration curve must be prepared daily and whenever the anion eluent is changed and after every 20 samples whichever is most frequent. If the response for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, an entire new calibration must be prepared for that analyte. Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum loading (all anions) should not exceed 400 ppm.

6.2.5 The width of the retention time window used to make identifications must be based upon measurements of actual retention time variations of standards run over three non-consecutive days. Three times the standard deviation will be used to calculate the retention time windows. The retention time for NO_2/NO_3-N must be within the retention time window established during the most recent initial calibration. A retention time window of 1% of the average retention time of the three standards must be used if the computed one is less than 1% of that average.

6.2.6 Load and inject a fixed amount of sample, using the same size loop for standards and samples. Flush the injection loop thoroughly, using each new sample. Record the resulting peak size in area or peak height units. An automated sampler system may be used.

6.2.7 If the response for the peak exceeds the linear range of the system, dilute the sample with an appropriate amount of reagent water (but not below the CRDL) and reanalyze.

7. CALCULATIONS

7.1 Prepare separate calibration curves for NO_2/NO_3-N by plotting peak size in area, or peak height units of standards against concentration. Compute sample concentration by comparing sample peak response with the standard curve.

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

7.3 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

8. QUALITY CONTROL

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

8.3 Reportable data for a sample must include a chromatogram with retention times within the retention time windows established during the most recent initial calibration. If identification of specific anions is questionable, the samples must be reanalyzed by other methods listed within this contract.

PART I
AUTOMATED COLORIMETRIC METHODS FOR THE DETERMINATION OF NO_2/NO_3-N

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of NO_2/NO_3-N in low concentration water samples.

1.2 The range of this method is 50 to 10000 ug/L NO_2/NO_3-N.

2. SUMMARY OF METHOD

2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically.

3. INTERFERENCES

3.1 Build up of suspended matter in the reduction column will restrict sample flow.

3.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.

3.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference can be eliminated by pre-extracting the sample with an organic solvent.

4. APPARATUS

4.1 Auto analyzer system with the following components:

4.1.1 Sampler.

4.1.2 Proportioning pump.

4.1.3 Nitrate-nitrite analytical cartridge.

4.1.4 Chart recorder.

4.1.5 Colorimeter with 50 mm tubular flow cell and 540 mm filter.

4.2 Operational Requirements

4.2.1 System Configuration -- 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 that particular instrument. Sensitivity,

instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for nitrate and nitrite on that particular instrument.

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 METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

5. **REAGENTS AND STANDARDS**

5.1 Granulated cadmium: 40-60 mesh.

5.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:

5.2.1 Wash the cadmium with 6N HCl and rinse with ASTM Type I water. The color of the cadmium so treated should be silver.

5.2.2 Swirl 10g cadmium in 100 mL portions of 2% solution of copper sulfate for five minutes or until blue color partially fades, decant, and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

5.2.3 Wash the cadmium-copper with ASTM Type I water (at least ten times) to remove all precipitated copper. The color of the cadmium so treated should be black.

5.3 Color reagent: To approximately 800 mL of ASTM Type I water, add, while stirring, 100 mL conc. phosphoric acid, 40g sulfanilamide, and 2g N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to one liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

5.4 Dilute hydrochloric acid, 6N: Dilute 50 mL conc. HCl to 100 mL with ASTM Type I water.

5.5 Copper sulfate solution, 2%: Dissolve 20g of $CuSO_4$-H_2O in 500 mL of ASTM Type I water and dilute to one liter.

5.6 Ammonium chloride-EDTA solution: Dissolve 85g of reagent grade ammonium chloride and 0.1g of disodium ethylenediamine tetracetate in 900 mL of ASTM Type I water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to one liter. Add 1/2 mL of a surfactant.

5.7 Stock standard solutions, 1000 mg/L (1mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as listed below.

5.7.1 Nitrate (NO_3-N) 1000 mg/L: Dissolve 6.0679g sodium nitrate ($NaNO_3$) in ASTM Type I water and dilute to one liter.

6. PROCEDURE

6.1 Calibration and Sample Analysis

6.1.1 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.

6.1.2 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

6.1.3 Prepare a blank and at least three standards over the suspected range of analysis. One calibration standard must be at the CRDL.

6.1.4 Samples must be neutralized (if the pH is below 5, from sulfuric acid preservation, or above 9) prior to analysis using either concentrated HCl or NH_4OH. The samples, standards, all QC samples, and dilution water must be matrix matched.

6.1.5 Place calibration standards, blanks, and quality control standards in the sampler tray, followed by samples.

6.1.6 When a steady baseline is obtained and before starting the sampler, adjust the baseline, using the colorimeter, to zero. Aspirate a calibration standard and adjust the colorimeter until the desired maximum signal is obtained. Re-establish the baseline and proceed to analyze the calibration standards, blanks, quality control standards, and samples.

6.1.7 Prepare standard curve by plotting absorbance peak heights of processed standards against known concentrations. The curve must have a correlation coefficient greater than or equal to 0.995. If the correlation coefficient is less than 0.995, the analysis must be repeated.

6.1.8 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte.

7. CALCULATIONS

7.1 Compute concentration of samples by comparing sample peak heights with standard curve.

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

7.3 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

8. QUALITY CONTROL

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

PART J
ION SELECTIVE ELECTRODE METHOD FOR THE DETERMINATION OF FLUORIDE

1. SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of fluoride in low concentration water samples.

1.2 The range of the method is 0.1 to 1000 mg/L of fluoride.

1.3 This method may not measure total fluoride.

2. SUMMARY OF METHOD

2.1 The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a potentiometric meter having an expanded millivolt scale.

2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions.

3. INTERFERENCES

3.1 Extremes of pH interference; sample pH should be between 5 and 9. Polyvalent cations of Silicon, Iron, and Aluminum interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.

4. APPARATUS

4.1 Selective ion meter

4.2 Fluoride Ion Activity Electrode

4.3 Reference electrode, single junction, sleeve type.

4.4 Magnetic stirrer, teflon coated stirring bar

4.5 Operational Requirements

4.5.1 System Configuration -- Because of the differences between various makes and models of satisfactory instruments, no detailed 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 fluoride on that particular instrument.

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 METHOD AND TO MAINTAIN QUALITY CONTROL DATA CONFIRMING INSTRUMENT PERFORMANCE AND ANALYTICAL RESULTS.

5. **REAGENTS AND STANDARDS**

5.1 **Buffer solution, pH 5.0 - 5.5:** To approximately 500 mL of distilled water in a 1 liter beaker add 57 mL of glacial acetic acid, 58 g of sodium chloride and 4g of CDTA (1,2-cyclohexylene dinitrilo tetraacetic acid). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (ABOUT 150 ML WILL BE REQUIRED). Transfer solution to a 1 liter volumetric flask and dilute to mark with ASTM Type I water.

5.2 **Fluoride (F^-) stock solution, 100 mg/L:** Dissolve .2210g of sodium fluoride in ASTM Type I water and dilute to 1 liter.

5.3 **Sodium hydroxide, 5 N:** Dissolve 200g sodium hydroxide in ASTM Type I water, cool and dilute to 1 liter.

6. **PROCEDURE**

6.1 **Calibration and Sample Analysis**

6.1.1 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.

6.1.2 Prepare at least four standards using the fluoride stock solution. The standards must be at the following concentrations: .1 mg/L, 1.0 mg/L, 2.0 mg/L, and at the CRDL. A blank standard does not need to be part of the calibration curve since the log of zero is undefined. However, a blank standard must be run immediately after calibration and it must yield a concentration value of less than 0.1 mg/L.

6.1.3 Place 50 mL of sample or standard solution and 50 mL of buffer in a 150 mL beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in solution and observe the meter reading while mixing. The electrodes must remain in solution for at least three minutes. Once the meter has stabilized, a reading may be obtained. At concentrations under 0.5 mg/L F, it may require five minutes or more to reach a stable meter reading.

6.1.4 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte.

7. CALCULATIONS

7.1 Using semilogarithmic graph paper, plot the concentration of fluoride in ug/L on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. If the instrument has the capability, fluoride concentration may be read directly from the meter.

7.2 If dilutions were performed, the appropriate factor must be applied to the sample value.

7.3 Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples, NO other units are acceptable.

8. QUALITY CONTROL

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

8.2 All quality control (QC) data must be submitted with each data package as specified in Exhibit B.

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. ICP/MS Tuning and Mass Calibration
2. Retention Time Window for Ion Chromatography
3. Instrument Calibration
4. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
5. CRDL Standards (CRI)
6. Linear Range Standard Analysis (LRS)
7. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
8. ICP and ICP/MS Interference Check Sample (ICS) Analyses
9. Matrix Spike Sample Analysis (S)
10. Duplicate Sample Analysis (D)
11. Laboratory Control Sample (LCS) Analysis
12. Performance Evaluation Sample (PES)
13. Serial Dilution Analysis (L)
14. Internal Standards for ICP/MS
15. Instrument Detection Limit (IDL) Determination
16. Interelement Corrections for ICP and ICP/MS
17. Hydride ICP (HYICP) and Furnace AA QC Analysis

1. ICP/MS TUNING AND MASS CALIBRATION

1.1 Guidelines for mass calibration and tuning are given in Exhibit D. Resolution and mass calibration must be performed for each ICP/MS system, each time the instrument is set up. The resolution and mass calibration must be verified immediately before instrument calibration. The resolution and mass calibration must also be verified at the end of each analytical run, or every eight hours, which ever is more frequent. The tuning solution must be analyzed after the final CCV/CCB in the run. The mass calibration and tuning times as well as their verification times must be included in the raw data.

A 100 ppb solution of elements Li, Co, In, and Tl must be used as a tuning verification solution. The intensities and isotopic ratios of the tuning criteria are as recommended in Table VIII, Exhibit C. The resolution and mass calibration criteria must be within the control limits in Table VIII, Exhibit C. If not, the analysis must be terminated, the problem corrected and all measurements taken by the instrument since the last compliant mass calibration and resolution check must be reperformed in a new analytical run.

1.2 The values for the initial and subsequent mass calibrations and resolution check shall be recorded on Form XIV - LCIN for ICP/MS analyses, as indicated in Exhibit B.

2. RETENTION TIME WINDOW FOR ION CHROMATOGRAPHY

2.1 Retention time windows for all analytes analyzed using Ion Chromatography (IC) must be established prior to any sample analysis and each time a new column is installed. The width of the retention time window used to establish identification must be based upon measurement of actual retention times of standards run over three non-consecutive days. The concentration of each standard must be sufficient to produce a response for each analyte that is approximately half scale. Three times the standard deviation of the retention time of the standards shall be used to calculate the retention time windows for each analyte. A retention time window of 1% of the average retention time of the three standards must be used if the computed one is less than 1% of that average.

The retention time window must be individually determined for each analysis run by measuring the retention time of the calibration standard near the mid range of the calibration curve for that run and making that retention time the center of the established retention time window (see Exhibit B). The retention time of each measured value for each analyte must be within the retention time window established during the most recent instrument calibration for that analyte. If not, the analysis must be stopped, the problem corrected, the instrument recalibrated, new retention time windows determined, and the samples analyzed since the last compliant CCV must be reanalyzed in a new run.

Retention times must be calculated and reported for each measurement taken for each analyte analyzed by IC.

2.2 The values for the retention time and retention time windows must be reported on Form XVII - LCIN for all analytes analyzed by IC systems, as indicated in Exhibit B.

3. INSTRUMENT CALIBRATION

3.1 Guidelines for instrumental calibration are given in EPA 600/4-79-0201 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours (8 hours for ICP/MS) and each time the instrument is set up. The instrument standardization date and time must be reported in the raw data.

Calibration standards must be prepared by diluting the stock solutions at the time of analysis, and be discarded after use. The date and time of preparation and analysis of the standards must be reported in the raw data.

The calibration standards must be prepared using the same type of matrix and at the same concentration as in the preparation blank following preparation. Aspirate, inject, or immerse the electrodes in

the calibration solutions as described in the individual methods (see Exhibit D), and record the readings for each analyte at each wavelength, mass, detector configuration, and potential used for analysis in the SDG.

Calibrate all systems according to the instrument manufacturer's recommended procedures or as specified in Exhibit D. At least one blank and a standard must be used for ICP, HYICP, and ICP/MS systems. All other systems must have a calibration standard at the CRDL, a blank, and at least two other standards. Systems that use non-linear calibration curves must use at least three additional standards which cover both the upper and lower ranges of the curve.

All calibration curves must have a correlation coefficient of 0.9950 or greater before any analysis may be started. The correlation coefficient for each calibration curve must be clearly documented and must be submitted with the raw data.

3.2 Baseline correction is acceptable as long as it is performed after each and every sample, or after the continuing calibration verification and blank check.

4. <u>INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)</u>

4.1 Initial Calibration Verification (ICV)

4.1.1 Immediately after each of the analysis systems have been calibrated, the accuracy of the initial calibration must be verified and documented for each and every analyte by the analysis of Initial Calibration Verification Solution(s). When resulting measurements exceed the control limits of Table III-Initial and Continuing Calibration Verification and CRDL Standard 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 Initial Calibration Verification Solution(s) are not provided, or where a certified solution of an analyte is not available from any source, analyses must be conducted on an independent standard at a concentration other than that used for regular 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, HYICP, ICP/MS and AA the Initial Calibration Verification Solution(s) must be run and reported at each wavelength and elemental expression used for analysis. For cyanide, the initial calibration verification standard must be distilled. The Initial Calibration Verification for cyanide serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association

with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV.

4.2 Continuing Calibration Verification (CCV)

4.2.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard solution must also be analyzed at the beginning of the run and after the last analytical sample.

4.2.2 If more than one wavelength or elemental expression is used to produce results for an analyte, the continuing calibration verification must be analyzed and reported for every wavelength and elemental expression used to produce results for that analyte in the SDG.

4.2.3 The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near (±10%) the mid-range levels of the calibration curve:

1. Provided solutions
2. A Contractor-prepared standard solution

The same continuing calibration standard must be used throughout the analysis runs for an SDG received.

4.2.4 Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples 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 smallest difference in time between any two consecutive analytical samples associated with the CCV.

4.2.5 If the deviation of the continuing calibration verification is greater than the control limits specified in Table III in Exhibit C, the analysis must be terminated, the problem corrected and the CCV reanalyzed only once. If the first reanalysis yields a CCV value within control limits, then the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification may be reanalyzed for the analytes affected. Otherwise the instrument must be recalibrated, the calibration verified and the affected analytical samples rerun in the context of a new run. If the affected analytical sample is an instrument

related QC sample such as ICS, CRI, or LRS, then the correction to the problem and reanalysis of the standards must be done immediately within the 8 hour limit for those standards. If not, reanalysis of all samples and QC samples in the run is required.

4.2.6 Each analytical sample must be preceded by a CCV. As many as ten (10) analytical samples may be analyzed before a subsequent CCV is required. However, the CCV must be reanalyzed within two (2) hours. The values for each analyte in the two CCVs must be within the control limits.

4.3 The values for the initial and subsequent continuing calibration verification must be recorded on Form II - LCIN for all analysis systems, as indicated in Exhibit B.

5. CRDL STANDARD (CRI)

5.1 To verify linearity near the IDL for all analysis systems, the Contractor must analyze a standard at two times the CRDL at the beginning and end of each sample analysis run, or a minimum of twice per 8 consecutive hours, whichever is more frequent, but not before Initial Calibration Verification. The CRI standard must be run for each analyte at every wavelength and elemental expression used for analysis.

5.2 All results for the analysis of the CRDL standard must fall within the control limits specified in Table III in Exhibit C for each analyte at every wavelength and elemental expression used for analysis. If not, the analysis must be terminated, the problem corrected and all analytical samples since the last compliant CRI reanalyzed.

5.3 The values for the initial and subsequent CRDL standards must be recorded on Form III - LCIN for all analysis systems, as indicated in Exhibit B.

6. LINEAR RANGE ANALYSIS STANDARD (LRS)

6.1 To verify the upper limit of the linear range of all analysis systems, the Contractor must analyze a standard at the upper limit of the linear range of ICP, HYICP, and ICP/MS systems and at the concentration of the highest calibration standard for all other analysis systems. The linear range standard must be analyzed at the beginning and end of each sample analysis run, or a minimum of twice per 8 consecutive hours, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run for each analyte at every wavelength or elemental expression used for analysis.

6.2 Results for the analysis of the LRS must fall within the control limits of ±10% of the true value for each analyte at every wavelength and elemental expression 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 values for the initial and subsequent linear range standards must be recorded on Form IV - LCIN for all analysis systems, as indicated in Exhibit B.

7. INITIAL CALIBRATION VERIFICATION BLANK (ICB), CONTINUING CALIBRATION VERIFICATION BLANK (CCB), AND PREPARATION BLANK (PB) ANALYSES

Three types of blanks are used for analysis. The calibration blank is used in establishing and checking the calibration curve, the preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure, and the rinse blank (if appropriate) is used to flush the system between all samples and standards.

7.1 Initial Calibration Verification Blank (ICB) and Continuing Calibration Verification Blank (CCB) Analyses

7.1.1 A calibration blank must be analyzed for each analyte at each wavelength and elemental expression used for analysis, immediately after each and every initial and continuing calibration verification, linear range standard and memory test solution (MTS), see Exhibit D (Part E) and Exhibit C (Table IX), at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run.

7.1.2 If more than one wavelength or elemental expression instrument setting is used to produce results for an analyte, the Initial and Continuing Calibration blanks must be analyzed and reported for every wavelength and elemental expression used to produce results for that analyte in the SDG.

7.1.3 If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported on Form V - LCIN. If the absolute value of the blank result exceeds the CRDL, analysis must be terminated, the problem corrected, the instrument recalibrated and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank must be reanalyzed. The instrument must be recalibrated, the calibration verified and the affected analytical samples rerun in the context of a new run. If any of the affected analytical samples are instrument related QC samples, such as ICS, CRI, LRS, or MTS, then the correction to the problem and reanalysis of the standards must be done immediately within the 8 hour limit for those standards. If not, reanalysis of all samples and QC in the run is required.

7.1.4 Each analytical sample must be preceded by a calibration blank. As many as ten (10) analytical samples may be analyzed before a subsequent CCB is required. However, the CCB must be reanalyzed within two (2) hours. The absolute value for each analyte in these two CCBs must fall below the CRDL.

For ICP/MS systems, the flush time between any of the samples in a run cannot be less than the flush time between the MTS and the CCB that immediately follows it in the memory test for that run. For all other analysis systems, the flush time between any of the samples in a run cannot be less than the flush time between the LRS and the CCB that immediately follows it in that run.

For all analysis systems, 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. A QC set is the set of analytical samples analyzed between two consecutive CCV/CCB sets.

Dry burns for Graphite Furnace AA are included in the flush time. Rinses and other similar activities are also included in the flush time for the purpose of this rule.

7.2 Preparation Blank (PB) Analysis

7.2.1 At least one preparation blank (or reagent blank), consisting of ASTM Type I water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch[1] of samples prepared, whichever is more frequent.

7.2.2 If more than one preparation blank for the same method was required, then the first batch of samples is to be associated with preparation blank one, the second batch of samples with preparation blank two, etc. Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

The preparation blanks are to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

1) If the absolute value of the concentration of the preparation blank is less than or equal to the CRDL (Exhibit C), no correction of sample results is performed.

2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the

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

associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte. The sample concentrations are not to be corrected for the blank value.

3) If an analyte concentration in the blank is below the negative CRDL, then all samples associated with the blank with analyte concentration less than 10x CRDL must be redigested and reanalyzed.

7.2.3 The values for the initial and continuing calibration blanks as well as the preparation blank must be recorded on Form V - LCIN for all analysis systems, as indicated in Exhibit B.

8. ICP AND ICP/MS INTERFERENCE CHECK SAMPLE (ICS) ANALYSIS

8.1 To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Sample at the beginning and end of each analysis run or a minimum of twice per 8 consecutive hours, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Sample must be obtained from EMSL/LV if available and be analyzed according to the instructions supplied with the ICS.

The Interference Check Sample consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB contains both the analytes and the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths and elemental expressions used for each analyte reported by ICP and ICP/MS.

The magnitude (absolute value) of the result of each non-interfering analyte for the analyses of Solution A for ICP and ICP/MS systems may not exceed the CRDL.

Results for the analyses of Solution AB during the analytical runs must be within the control limit of ±20% of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last compliant ICS.

If the ICP Interference Check Sample is not provided, independent ICS must be prepared with interferent and analyte concentrations at the levels specified in Table V-Initial and Continuing Calibration Verification and CRDL Standard Control Limits For Inorganic Analyses (see Exhibit C).

If the concentrations of the interfering analytes in Solution A or AB are above the linear range of the instrument, diluting those solutions is permitted as long as the dilution does not cause the true value of the interfering analytes to be less than 10% of the established linear range.

8.2 The values for the ICP and ICP/MS interference check sample must be recorded on Form VI - LCIN for all analysis systems, as indicated in Exhibit B.

9. MATRIX SPIKE SAMPLE ANALYSIS (S)

9.1 The matrix spike sample analysis is intended to provide information about the effect of the sample matrix on the preparation and measurement methodology. The spike is added before the sample preparation (i.e., prior to digestion or distillation). One spike sample analysis per method must be performed on each group of samples for each Sample Delivery Group.

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 10, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks must not be used for spiked sample analysis. SMO may require that a specific sample be used for the spike sample analysis. This requirement is indicated on the traffic report or other documents that are shipped to the Contractor with the samples, and must be followed.

For Spike Sample Analysis each analyte must be spiked with a concentration level in the Spiked Sample solution as indicated in Table IV in Exhibit C.

If two analytical methods are used to obtain the reported values for a given analyte within a Sample Delivery Group, then spike samples must be run by each method used.

If the spike recovery is not within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on Form I- LCIN and VII - LCIN. An exception to this rule must be followed when the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data must be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

In the instance when there is more than one spike sample per method per SDG, if one spike sample recovery is not within the control limits, all samples of the same method in the SDG must be flagged.

Individual component percent recoveries (%R) are calculated as follows:

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

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

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive, negative or zero) must be reported on Form VII - LCIN for all analysis systems, as indicated.

9.2 The values for the sample, spiked sample and the spike added shall be recorded on Form VII - LCIN for all analysis systems, as indicated in Exhibit B

10. DUPLICATE SAMPLE ANALYSIS (D)

10.1 One duplicate sample per method must be analyzed for each Sample Delivery Group. Duplicates cannot be averaged for reporting on Form I - LCIN.

Samples identified as field blanks must not be used for duplicate sample analysis. SMO may require that a specific sample be used for duplicate sample analysis. This requirement is usually indicated on the traffic report and must be followed. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group, duplicate samples must be run by each method used.

The relative percent differences (RPD) for each analyte are calculated as follows:

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

Where, RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

A control limit of 20% for RPD must be used for original and duplicate sample values greater than or equal to 5x IDL. A control limit of (±) the IDL must be used if either sample or duplicate values is less than 5x IDL, and the absolute value of the control limit (IDL) must be entered in the "Control Limit" column on Form VIII - LCIN.

If one result is above the 5x IDL level and the other is below, use the ± IDL criteria. If both sample values are less than the IDL, the RPD is not reported on FORM VIII - LCIN.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms I - LCIN and IX - LCIN. 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 method in the SDG.

10.2 The values for the sample and duplicate must be recorded on Form VIII - LCIN for all analysis systems, as indicated in Exhibit B.

11. LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

11.1 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 field samples received.

The LCS will be provided for a period of at least nine months after contract award. The LCS must be prepared and analyzed using each of the procedures applied to the analysis of field samples. If the LCS is unavailable, other quality assurance check samples or certified materials traceable to NIST certified standards may be used. The true value for each analyte concentration in the LCS must not exceed the instrument's linear range and must not be added at a concentration lower than the contract required detection limit (CRDL) for that analyte. One LCS must be prepared and analyzed for each group of samples in a Sample Delivery Group, or for each batch of samples prepared by the same method, whichever is more frequent.

If the results of the LCS are outside the control limits established by SMO, the analysis must be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed. A control limit of ±20% of the true value must be used if no control limits are provided with the LCS solution.

11.2 The values for the LCS must be recorded on Form IX - LCIN for all analysis systems, as indicated in Exhibit B, Section II.

12. PERFORMANCE EVALUATION SAMPLE (PES)

12.1 The Performance Evaluation Sample will assist SMO in monitoring contractor performance. The PES may be designated as a single blind QC material or as full volume samples along with other environmental samples as a double blind. The laboratory will not be informed of the analytes in the PES or their concentration and the PES will be analyzed concurrently with all samples in the Sample Delivery Group.

The Contractor must dilute the PES to volume according to the instructions that accompany the ampules to the laboratory.

The laboratory must prepare the samples for analysis using the sample preparation procedures outlined in Exhibit D, Section III, Sample Preparation. The PES will be analyzed as a TOTAL CONSTITUENT ANALYSIS. Analysis of the PES will be in accordance with Exhibit D, Section IV, Sample Analysis. All contract QC must also be met.

In addition to PES dilution, preparation and analysis, the Contractor will be responsible for correctly identifying and quantifying the analytes included in the PES. SMO will notify the Contractor of unacceptable performance. NOTE: Unacceptable performance for identification and quantification of analytes in the PES is defined as a score of less than 75 percent.

12.2 The analysis results for the PES must be recorded on Form I - LCIN for all analytes. Exhibit B, Section II explains the instructions for completing the forms.

13. SERIAL DILUTION ANALYSIS (L)

13.1 In order to check for the presence of matrix interference, the Contractor must analyze and report the results of the Serial Dilution analysis. Except for HYICP, ICP/MS, and Furnace AA methods, one Serial Dilution analysis per method must be performed for each Sample Delivery Group. Identified field blanks may not be used for Serial Dilution analysis.

The Serial Dilution analysis is performed by diluting a prepared sample aliquot five-fold (5x or 1+4). The dilution must be performed on an analyte by analyte bases. The serial dilution is the dilution of the sample, or an aliquot of the sample, that contains a concentration level of the analyte within the linear range.

If the analyte concentration in the field sample is sufficiently high (minimally a factor of 50 above the IDL), the Serial Dilution must agree within 10% of the initial sample concentration determination after correction for the five fold dilution. If the Serial Dilution analysis for one or more analyte is not within 10%, a chemical or physical interference effect must be suspected and the data for all analytes exceeding the limit in the samples associated with that serial dilution must be flagged with an "E" on Form X - LCIN and Form I - LCIN.

13.2 The values for the Initial sample and serial dilution must be recorded on Form X - LCIN for all analysis systems, as indicated in Exhibit B.

14. INTERNAL STANDARDS FOR ICP/MS

14.1 In order to check for the presence of physical interferences and correct for them, the contractor must use, measure, and report the results of the internal standards for each ICP/MS analysis performed.

A minimum of three internal standards, listed in Table X Exhibit C, bracketing the mass range must be used. The intensity level of an internal standard for each sample, duplicate, spike analysis and PES must be greater than 30% and less than 125% of the intensity level of the internal standard of the blank calibration standard solution (SO). If not, the sample must be reanalyzed after performing a five fold (1+4) dilution. If the percent relative intensity, %R, (see Exhibit B, Part Q) remains less than 30% or greater than 125%, a physical interference must be suspected, and the data on Form XV must be flagged with an "E". The analytes affected by the interference must be flagged with an "E" on Form I - LCIN. The analytes affected by the interference must be listed in the comment section on the appropriate Forms VII - LCIN and VIII - LCIN if the affected sample is a matrix spike or duplicate.

The intensity levels of the internal standards for the CCV and CCB solutions must agree within ±20% of the intensity level of the internal standard of the initial calibration blank standard solution (SO). If not, the analysis must be terminated, the problem corrected and the CCV/CCB reanalyzed only once. If the reanalysis of a CCV/CCB yields a %R value within control limits, then the analysis must be stopped, the problem corrected, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification may be reanalyzed for the analytes affected. Otherwise, the instrument must be recalibrated, the calibration verified and the affected analytical samples rerun in the context of a new run.

The intensity levels of the internal standards for the ICV and ICB solutions must agree within ±20% of the intensity level of the internal standard of the blank calibration standard solution (SO). If not, the analysis must be terminated, the problem corrected, and a new analytical run must be started.

14.2 The values for the Internal Standard Percent Relative Intensity (%R) must be reported for each ICP/MS analysis on Form XV - LCIN as indicated in Exhibit B.

15. INSTRUMENT DETECTION LIMIT (IDL) DETERMINATION

15.1 Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must have been determined for each instrument used, no earlier than 30 calender days before the start of contract analyses and at least quarterly (every 3 calendar months thereafter), and must meet the levels specified in Table I in Exhibit C.

If a Contractor fails to adhere to the requirements listed in this section, a Contractor may expect, but SMO is not limited to the following actions: reduction of numbers of samples sent under this contract, suspension of sample shipment to the Contractor, ICP/MS tape audit, data package audit, an on-site laboratory evaluation, remedial performance evaluation sample, and/or contract sanctions.

The Instrument Detection Limits (in ug/L) must be determined by multiplying by three the average of the standard deviations obtained on three nonconsecutive days (each analyte in reagent water) at a concentration 3 times or 5 times the IDL, with seven consecutive measurements. 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). IDLs must be determined and reported for each set of instrument parameters used in the analysis of samples, including wavelengths in ICP, and elemental expressions in ICP/MS.

The quarterly determined IDL for an instrument must be used as the IDL for that instrument during that quarter. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on Form XII - LCIN and submitted with each data package. If multiple instruments are used for the analysis of an analyte within a Sample Delivery Group, the highest IDL for the analyte must be used for reporting concentration values for that Sample Delivery Group.

The Instrument Detection Limit for each analyte must be less than or equal to the Contract Required Detection limit. An exception is granted if the analyte concentration in the samples analyzed by an instrument is greater than or equal to five times the reported detection limit for that instrument.

15.2 Instrument Detection Limits must be determined quarterly. The results of that determination must be reported on Form XII - LCIN, and submitted with each data package, for each and every instrument used to produce data in the SDG, as indicated in Exhibit B.

16. INTERELEMENT CORRECTIONS FOR ICP AND ICP/MS

16.1 The ICP and ICP/MS interelement correction factors must have been determined within three months prior to beginning sample analyses under this contract, and at least annually thereafter. Correction factors for spectral and isobaric interferences must be determined at all wavelengths and elemental expressions used for each analyte reported by ICP and ICP/MS.

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 interelement correction factors, the factors must be redetermined and the results submitted for use.

16.2 Interelement correction factors must be determined annually. The results of that determination must be reported on Form XIII - LCIN, and submitted with each data package, for all ICP and ICP/MS parameters, for each and every instrument used to generate data in the SDG, as indicated in Exhibit B.

17. HYDRIDE ICP (HYICP) AND FURNACE AA QC ANALYSES

Because of the nature of the HYICP and Furnace AA techniques, the procedures summarized in Figure 1 are required for quantitation. (These procedures do not replace those in Exhibit D, but supplement the guidance provided therein).

a. All results of HYICP and Furnace AA analyses must be within the linear and calibration range respectively. In addition, all results of analyses, except during full Methods of Standard Additions (MSA), require duplicate exposures (injections for Furnace AA). Average concentration values must be used on the Reporting Forms. A maximum of 10 full sample analyses to a maximum 20 exposures or injections may be performed between each consecutive calibration verification and blank. The raw data package must contain intensity (absorbance for Furnace AA) and concentration value for both exposures (injections for Furnace AA), the average value and the relative

standard deviation (RSD) or coefficient of variation (CV) for each analysis. For concentrations greater than IDL, the duplicate exposure (injections for Furnace AA) readings must agree within 15% RSD or CV, or the analytical sample must be rerun once (i.e., two additional exposures or injections). If the readings are still out of the 15% limit, flag the value reported of Form I - LCIN 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 - LCIN for that sample.

b. All HYICP and Furnace AA 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[2] will be required to be at a concentration (in the sample) of 30% of the linear range of each analyte. This requirement for an analytical spike will include the LCS and the preparation blank. The LCS must be quantified from the calibration curve and corrective action(i.e. redigestion), if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control limits, the problem must be corrected and respiking and reanalysis of all analytical samples associated with that blank must be performed. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see Section 9), determines how the sample will be quantified, as follows:

1) If the spike recovery is less than 40%, the sample must be diluted by a factor of 5 and rerun with another spike. This step must only be performed once. If, after the dilution, the spike recovery is still <40%, report data from the initial undiluted analysis and flag with an "E" to indicate interference problems.

2) If the spike and the spike recovery is at or between 85% and 115%, the sample must be quantified directly from the calibration curve and reported down to the IDL.

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[2]Analytical spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the prepared sample. The unspiked sample aliquot must be compensated 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% of the analytical sample volume. This requirement also applies to MSA spikes.

3) If the spike recovery is greater than 40% and less than 85%, or greater than 115%, the sample must be quantified by MSA.

c. The following procedures must be incorporated into MSA analyses.

1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data are specifically excluded from use in the MSA quantitation). Only single exposures (injections for Furnace AA) are required for MSA quantitation.

Each full MSA counts as two analytical samples toward determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

3) For analytical runs containing only MSAs, single exposures (injections for Furnace AA) 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. This option must be used consistently.

4) Spikes must be prepared such that:

a) Spike 1 is approximately 50% of the sample concentration in ug/L.

b) Spike 2 is approximately 100% of the sample concentration in ug/L.

c) Spike 3 is approximately 150% of the sample concentration in ug/L.

5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and intensity or found concentration as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data, the results must be reported on Form XI - LCIN. Reported values obtained by MSA must be flagged on the data sheet (Form I - LCIN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.

6) If the correlation coefficient (r) for an MSA 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 - LCIN from the run with the greater correlation coefficient "r" and flag the result with a "+". On Form XI - LCIN report the results of both MSA analysis and flag with a "+" for any MSA result that yields a correlation coefficient less than 0.995.

Figure 1
FURNACE ATOMIC ABSORPTION AND HYICP
ANALYSIS SCHEME