MRI

QUALITY ASSURANCE MANUAL

Inductively Coupled Plasma Atomic Emission Spectrometry for Toxic Trace Metals in Vegetables, Soils, and Sludges

in

The National Household Garden Survey

by

Lloyd M. Petrie
Senior Chemist

EPA Contract No. 68-01-5915
MRI Project No. 4901-A(42)

May 26, 1982

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I. Introduction

The Field Studies Branch is conducting a nationwide survey of household gardens fortified with POTW (publicly owned treatment works) sewage sludge to assess level of pesticides, metals, and parasites in the soils and vegetables. Approximately 240 garden sites will be sampled during the 1982 growing season.

Toxic metals are relatively abundant in municipal sewage and tend to accumulate in high levels in the resulting sewage sludge in parts per million levels (Page and Chang, 1978; Swanson, 1981). One means of disposal of the large quantities of sewage sludge is to use it as a fertilizer for cultivation of edible food crops.

Nationally, a key concern regarding cropland fertilization with sewage sludge is the rate of uptake of toxic trace metals into the food crops. This potential problem has been and is being studied to determine safe levels of sewage sludge application (Page and Chang, 1978; Page, 1978; Naylor and Loehr, 1981; Stoewsand, 1980; Garcia et al., 1981). Page and Chang (1978) cite Cd, Cu, Mo, Ni, and Zn as the trace metals of greatest concern due to their abundance in sewage sludge and their mobility in soils. Stoewsand (1980) cited As, Sb, Pb, Hg, and Pd of greatest human health concern with Pb and Cd being the most important toxic elements in sewage sludge cropland disposal due to their abundance and soil mobility. Of these two, Cd is more readily taken up by plants. The large survey by Garcia et al. was concerned with soil and plant concentration of Pb, Hg, Cd, and Zn. Again, Cd was significantly accumulated in a wide range of edible crops. Therefore, the MRI trace metal analysis of vegetables, soils, and sludges will include the following key target trace elements Cd, Pb, Cu, Mo, Ni, As, Sb, Hg, and Zn. Also analyzed will be Sn, Tl, Co, Be, B, Mn, Cr, Ag, Y, Se, and Ba.

Determination of trace metals in this study will be accomplished by first solubilizing the metals into an acidic medium from the solid samples. Then, the ICP media will be quantitatively analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). ICP emission spectrometry is a rapid technique that is well-suited to multielemental analysis survey work.

The purpose of this document is to detail the quality assurance program for ICP-AES to be followed during this study. It is designed to assure ICP-AES analytical data with acceptable accuracy and precision in a cost-effective manner. Likewise, the plan is designed to ensure proper handling and control of samples and all written documentation.

The analytical quality control aspects of this manual conform to the USEPA Interim Method 200.7, "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Analysis of Water and Wastes," EPA-EMSL, Cincinnati, November 1980. Appendix A contains a copy of this method.

II. Quality Assurance Objectives

The objective for accuracy is percent recovery values for all analyte metals in fortified samples between 80% and 120%.

The objective for precision is percent relative standard deviation values for all analyte metals in duplicated samples between 0% and 10%.

III. Personnel Responsibilities

John Hosenfeld will be the task leader for this program. He will:

* Supervise the collection of all field samples and their transport to MRI.
* Oversee conformance to the policies and procedures stated in this Quality Assurance Plan.
* Review and accept each set of analytical data in view of the quality assurance objectives for ICP-AES metals screen.
* Monitor the technical progress of the program against financial expenditures.

Lloyd Petrie will be the trace metal analysis leader. He will:

* Direct conformance to the policies and procedures stated in this Quality Assurance Plan.
* Schedule the preparation and analysis of all field and quality control samples.
* Provide technical expertise for sample preparation and ICP emission spectrometric analysis.
* Prepare USEPA AQC standard for validation of instrument calibration standards.
* Maintain document control of laboratory data, field data, notes, records, etc.
* Be responsible for sample log-in and chain of custody.
* Enforce instrument calibration and maintenance procedures and schedule.
* Technically review all analytical data reported to the task leader.
* Provide technical expertise for operation of the Digital Equipment Corporation (PDP 11/23) computer.

* Immediately report in memo form any problems which arise during the course of the program to the task leader.

Gene Ray will be the quality assurance coordinator. He will:

* Prepare blind duplicate samples for sample preparation of both soils and vegetables.

* Prepare blind analytical quality control standards for all ICP-AES analyses.

Carolyn Thornton will be the ICP-AES trace metal analyst. She will:

* Perform ICP-AES analysis of all samples according to the procedures stated in this Quality Assurance Plan.

* Prepare analysis quality control standards and samples according to the Quality Assurance Plan procedures.

* Prepare instrument calibration standards according to the Quality Assurance Plan procedures.

* Generate, store and retrieve all analysis documentation according to the Quality Assurance Plan procedures.

* Handle prepared digests and leachates according to sample custody procedures stated in the Quality Assurance Plan.

* Be responsible for routine maintenance of the ICP emission spectrometer.

Betty Jones will be the sample preparation analyst. She will:

* Retrieve and handle all field samples according to this Quality Assurance Plan sample custody procedures.

* Clean and label all glassware or plasticware used in sample preparation according to procedures stated in this Quality Assurance Plan.

* Prepare all field samples and related quality control samples according to the appropriate sample preparation procedures.

* Generate, store and retrieve all sample preparation documentation according to the Quality Assurance Plan procedures.

IV. Analytical Methods

A. Sample Container Cleaning

1. Objective: To remove all trace metal contamination from the surface of all plastic or glass containers used for sample handling.

2. Procedures

a. Wash only those glass centrifuge tubes containing organic residues with freshly prepared soapy deionized water. Do not wash plastic bottles with soap.

b. Rinse the soap from the containers thoroughly with deionized water.

c. Soak both glass and plastic containers in 8 N reagent grade HNO_3 for 24 hr. Prepare a fresh 8 N reagent grade HNO_3 bath every 2 weeks.

d. After 24 hr, remove and thoroughly rinse the containers with deionized water. At least six rinses will be necessary.

e. Dip the Teflon-lined centrifuge tube caps in the 8 N HNO_3 acid bath, remove immediately, and thoroughly rinse with deionized water.

f. Fill each container with 0.5 N double-distilled HNO_3 and tightly cap the containers. Let the container stand at least 12 hr.

g. Empty and rinse the containers six times with laboratory deionized water.

h. Shake out remaining water, cap, and store the containers in a clean drawer.

3. Time/material requirements: Approximately 4 hr per batch of preparation samples should be adequate for sample container cleaning.

Copies of purchase requisitions or supply room orders should be submitted to the metal analysis leader.

B. Plant Digestion

1. Objective: To fully solubilize the entire plant tissue by a wet acid digestion.

2. Procedures

a. Sample preparation sheet: A "SAMPLE PREPARATION SHEET" (Figure 1) will be completed in duplicate by the trace metal analysis leader. The following conventions will be used:

Digestion Code:

V (vegetable)	nn	incremented digestion number (nn) of type preparation starting with Ø1
S (soil)	nn	
L (sludge)	nn	

Sample Names:

Field samples (6-number code)

Example:	01	107	2	= soil
	Digestion Number	Sample Number	5	= sludge
			7	= vegetable
			Sample Type	

Analytical quality control standards (6 alphanumeric code): AQC1, N476E2

Prepared reagent blank (6 alphanumeric code): VnnRBm - incremental number (m); Digestion Code

Class Names (6 alphanumeric code):
RB - prepared reagent blank
SAMPLE - prepared field sample
DUP - duplicate
SP1 or SP2 - fortified sample at level "1" or "2"
SRM1 or SRM2 - standard reference material "1" or "2"

b. Sample drying

(1) Field vegetable samples should be dried within 1 week of receipt at MRI.

(2) Place a representative portion of each vegetable in a clean porcelain dish or glass beaker.

(3) Dry the samples for 4 hr at 90°C.

(4) Remove the dried samples and let them cool to room temperature.

(5) Place the dried material in clean 30-ml plastic bottles, each labeled with the field sample number, sample type and date.

SAMPLE PREPARATION SHEET

Project No.:_____ Digestion Code:_____

Elements:_____

Analyst:_____

Date Begun:_____ Date Completed:_____

Prep Description:

Sample Volume (ml or mass/g):_____

Fortification Levels (total g):_____

Digest Final Volume (ml):_____

	Sample	Class	Sample	Final Wt.		Sample	Class	Sample	Final Wt.
1.					26.				
2.					27.				
3.					28.				
4.					29.				
5.					30.				
6.					31.				
7.					32.				
8.					33.				
9.					34.				
10.					35.				
11.					36.				
12.					37.				
13.					38.				
14.					39.				
15.					40.				
16.					41.				
17.					42.				
18.					43.				
19.					44.				
20.					45.				
21.					46.				
22.					47.				
23.					48.				
24.					49.				
25.					50.				

Figure 1

c. Wet digestion

(1) According to the "SAMPLE PREPARATION SHEET," label the needed number of clean 10-ml centrifuge tubes and 30-ml plastic bottles with the "Sample" and "Class" names.

(2) Weigh the tubes and bottles and record the tare weights.

(3) Place approximately 0.1 g dried vegetable in each preparation tube and weigh the actual amount added.

(4) Add 4.0 ml 8 N Meck Suprapur® HNO_3 to the tubes.

(5) Wrap the tube threads with Teflon® tape twice and seal the tube with a clean Teflon®-lined cap.

(6) Place the tube rack in a preheated oven at 90°C.

(7) Check the tubes after 1 hr and gently agitate the contents of each tube.

(8) Remove tubes after 4 hr at 90°C.

(9) Let the tubes air cool to room temperature.

(10) Dilute the samples in the tubes to 10 g with deionized water using the platform balance.

(11) Label each tube with the "Sample" name, "Class" name, "4901A42," and date.

(12) Place a copy of the completed "SAMPLE PREPARATION SHEET" in the appropriate MRI Technical Record Book and place the original sheet with the completed samples on a tray.

3. Quality control: Unless stated otherwise on the "SAMPLE PREPARATION SHEET" to reflect unique conditions, the following percentages of analytical quality control samples will be prepared with each batch of field samples:

10% duplicates of field samples
10% fortified field samples
5% reagent blanks
5% quality control check standards or standard reference materials
5% blind field duplicate samples selected by the quality assurance coordinator

4. Time/materials requirements: Sample drying should require 2 hr labor time per sample batch.

Wet digestion of a 50-sample set should require 8 hr labor time and should be fully completed during 1 day to minimize sample handling and contamination. Approximately 125 ml of Merck Suprapur® concentrated nitric acid will be the major material usage. The replacement frequency of the Teflon®-lined centrifuge caps is not known.

C. Soil and Sludge Leaching

1. Objective: To remove all trace metals from soil or sewage sludge using a rigorous acid leaching without solubilizing all the Al, Fe, Ca, Mg, Ti, and other nontoxic major elements in the samples.

2. Procedure

a. According to the "SAMPLE PREPARATION SHEET," label the needed number of clean 10-ml centrifuge tubes and 30-ml plastic bottles with the "Sample" and "Class" names.

b. Tare each centrifuge tube without the cap and record the mass.

c. Place approximately 0.1 g soil in the appropriate tubes and measure the net mass of sample added. Record the masses on the "SAMPLE PREPARATION SHEET."

d. Add 2 ml 8 N Merck Suprapur® HNO_3 to the appropriate tubes.

e. Wrap the tube threads with Teflon® tape.

f. Place the tube rack in a preheated oven at 130°C for 8 hr.

g. Set the timer on the oven electrical circuit for a time 8 hr hence.

h. Check the tubes every 2 hr and gently agitate the contents of each tube.

i. Remove the tubes after 8 hr of heating.

j. Let the tubes air cool to room temperature.

k. Dilute the material in each tube to a final net mass of 10 g with deionized water.

l. Centrifuge each set of four tubes at the maximum setting of the International Clinical centrifuge in Room 344W for 1 min.

m. Remove the centrifuged samples and carefully pour the liquid leachate into the appropriate plastic bottle.

n. Label each plastic bottle with the "Sample" name, "Class" name, "4901A42" and date.

o. Place a copy of the completed "SAMPLE PREPARATION SHEET" in the appropriate MRI Technical Record Book and place the original sheet with the completed samples on a tray.

3. Quality control: Unless stated otherwise, the following percentages of analytical quality control samples will be prepared with each batch of field samples:

10% duplicates of field samples
10% fortified field samples
5% reagent blanks
5% quality control check standards or standard reference materials
5% blind field duplicate samples selected by the quality assurance coordinator

4. Time/materials requirements: Acid leaching of each 50-sample set should require 8 hr labor time. Each preparation batch will consume approximately 75 ml of Merck Suprapur® concentrated nitric acid and Teflon® tape. The replacement frequency of the Teflon®-lined centrifuge caps is not known.

D. Inductively Coupled Plasma Atomic Emission Spectrometry

1. Objective: To quantitatively determine the concentration of toxic trace metals in soil, sludge, and vegetable preparations by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2. General description of method: ICP emission spectrometry is a relatively new method for rapid multielemental analysis using a new, stable excitation source (ICP) with the conventional direct reading or newer scanning spectrometers.

Compared to other sources, spectral interferences for the ICP are minimal. It is hot enough to facilitate analyte emission, yet the sustained argon plasma has fewer of the interferences associated with emission spectroscopy. The background in the region with most of the sensitive emission lines for many elements (190-300 nm) has relatively few interference emissions.

However, there still are spectral interferences that are significant when attempting to measure parts-per-billion levels of trace metals in the presence of parts-per-million levels of Al, Ca, Fe, Ti, and other major elements in plant and soil material. The two major types of spectral interferences are (1) direct overlap by an interfering emission peak on the analysis emission peak, and (2) baseline shifts due to stray light, molecular emission or broad band emission from an intense nearby interfering peaks.

To account for those cases where other elements may line interfere and are commonly abundant in high concentrations (Al and Fe, for example), correction factors are stored in a data file in the computer. As part of the final concentration calculations, a factor multiplied by the interfering element intensities is subtracted from the gross analyte intensities.

3. Instrument description: A 30-channel Jarrell-Ash Model 1155A direct reading ICP emission spectrometer will be used in the study. This instrument has the following features to enhance sample analysis quality:

* Triple point background correction
* Automatic interelement spectral interference correction
* Spectrum scanning for sample matrix diagnostics
* 200-Sample autosampler
* Peristaltic pump

The emission spectrometer is fully controlled by a sophisticated set of software performed at the Digital Equipment Corporation PDP 11/23 computer interfaced to the spectrometer.

Based on prior method development studies, Table 1 lists typical detection limits anticipated for this study for the 30 analytical emission lines of the Model 1155A spectrometer.

Two Analytical Control Tables will be used for this study:

ACT Name	Sample Matrix
VEG	Vegetables
SOIL	Soils and sludges

4. Daily instrument calibration procedure

a. Instrument calibration is based on Chapter 8 of the Jarrell-Ash Mark III Atomcomp Interim Operator's Manual, M79, March 1979. The analytical quality control aspects of calibration conform to USEPA Interim Method 200.7.

b. Each of the 30 detector channels is calibrated by a two-point curve method using a reagent blank and a 10-ppm standard, except 100 ppm for K. The elements for the 10-ppm standard are actually grouped into four mixed standards according to chemical stability and absence of spectral interferences. Table 2 shows the composition of the ICP-AES calibration standards.

c. It is essential that the matrix of the calibration standards match the matrix of the samples. In this study the following matrices for calibration standards will be used.

Vegetables	20% (v/v) Merck Suprapur® HNO_3
Soils and sludges	10% (v/v) Merck Suprapur® HNO_3

TABLE 1

AVAILABLE ANALYTICAL CHANNELS

Element	Wavelength (Å)	Estimated Detection Limit (µg/g sample)	
		Soil	Vegetable
Sn	1899	20	20
Tl	1908	70	10
As	1936	250	30
Hg	1942	20	5.0
Se	1960	1,000	100
Mo	2020	2.0	0.23
Sb	2068	200	100
Zn	2138	4.0	2.0
P	2149	20	96
Pb	2203	50	4.0
Co	2286	1.0	0.18
Cd	2288	2.0	0.14
Ni	2316	1.0	0.49
Be	2348	0.50	0.030
Al	2373	96	8.6
B	2496	1.0	0.75
Mn	2576	10	2.50
Fe	2599	350	6.0
Cr	2677	2.0	0.23
Fe	2714	20	5.7
Mg	2795	40	340
Al	3082	110	8.7
Cu	3247	2.0	0.54
Ag	3280	0.5	0.5
Ti	3349	20	2.0
Y	3710	3.0	0.043
Ca	3968	41	360
Ba	4934	5.4	0.16
Na	5890	10	290
K	7665	140	690

TABLE 2

ICP-AES CALIBRATION STANDARDS

Matrix: 20% (v/v) HNO_3 (vegetables) or 10% (v/v) HNO_3 (soils)
Concentration: 10 ppm except 100 ppmK
Stability: 30 days

Standard ID	Elements
STD 1	Reagent blank
STD 2	Ba, Ca, Cd, Co, Cu, K, Mg, Mn, Pb, Zn
STD 3	Al, Be, Fe, Mo, Na, Ni, Sb, Ti, Y
STD 4	As, B, Cr, P, Se, Sn, Hg, Tl
AG	Ag

d. The shelf life of the calibration standards is 30 days.

e. Each new batch of calibration standards that is prepared must be verified weekly for accuracy by analyzing a standard reference material and obtaining measured values within ± 5% of the certified values. See the section on "Analytical Quality Control."

f. The spectrometer is calibrated according to MRI Interim Standard Operating Procedure "ICP Emission Spectrometer Calibration."

5. Daily sample analysis procedure: After successful calibration, a prepared sample set can be analyzed. The Analytical Quality Control aspects of this procedure conform to USEPA Interim Method 200.7.

a. Fill out an "ICP DATA REPORTING SHEET" (Figure 2) and place it in the appropriate MRI Technical Record Book. In this study, a fixed crossflow nebulizer and peristaltic pump will always be used.

b. Aspirate each sample for 1 min.

c. Analyze one representative sample for one 10-sec integration without dilution factors to determine if any detection channels are beyond their linear response range (Table 3). If necessary, dilute the samples and note that on the "SAMPLE PREPARATION SHEET."

d. Every 10th time, reanalyze STD1 and the ICS, after thoroughly rinsing the nebulization system.

e. If the analytical results are still within ± 2 x standard deviation control limits, continue. If the results were out of control, reanalyze STD1. If the results are still out of control, recalibrate the instrument.

f. If the measured values for the ICS are still within ± 5% of the true values, continue. If not, reanalyze the ICS. If the results are again out of control, recalibrate the instrument.

g. All prepared samples analyzed since the last successful analysis of STD1 and the ICS must be reanalyzed if the instrument is recalibrated.

h. Place data, along with a copy of the "ICP DATA REPORTING SHEET" into the "Sample Analysis" blue multi-ringed binder for computer paper output.

ICP DATA REPORTING SHEET

Project No.:_____ Analyst:_____
Sample Matrix:_____ Date:_____
Elements:_____ Digestion Code:_____

Instrument Parameters

Forward Power (kw):_____ Coolant Gas Flow (ℓ/min): _____
Reflected Power (w):_____ Auxiliary Gas Flow (ℓ/min):_____
Observation Height (mm):___ Sample Gas Flow (ℓ/min):_____
Nebulizer Type:_____ Solution Uptake (ml/min):_____
(FCF = Fixed crossflow) Peristaltic Pump Used?:_____
(HS = High solids)

Sample Analysis

ACT Name:_____

Test Performed:___Spectrum Scan
Integration Time (sec):_____
Data Files:_____
_____
_____
_____
Disk Name: _____

___Quantitation and Log
Command String:_____
Data File Name:_____
Disk Name:_____

___Quantitation and Store
Command String:_____
Data File Name:_____
Disk Name:_____

Figure 2

TABLE 3

LINEAR RESPONSE RANGE OF THE ICP-AES CHANNELS

LCN	Channel	Linear Maximum Concentration (ppm)
2	Ag	100
3	Al (3082 Å)	200
4	Al (2373 Å)	150
5	As	500
6	B	100
7	Ba	50
8	Be	50
9	Ca	50
10	Cd	200
11	Co	100
12	Cr	50
13	Cu	150
14	Fe (2714 Å)	500
15	Fe (2599 Å)	30
16	Hg	500
17	K	500
18	Mg	20
19	Mn	50
20	Mo	50
21	Na	200
22	Ni	200
23	P	200
24	Pb	500
25	Sb	500
26	Se	200
27	Sn	500
28	Ti	50
29	Tl	200
30	Y	50
31	An	30

6. Analytical quality control

a. Spectral interferences

(1) The occurrence of spectral interferences in ICP source emission spectrometry is not as frequent as with other emission sources but is common enough to require correction measures. The "General description of method" section described the common types of spectral interferences experienced in ICP-AES: (a) direct overlap by an interfering emission peak, and (b) baseline shifts due to stray light and molecular emission. These interferences both result in falsely high analyte emission and, hence, analyte concentration determinations.

(2) The particular sample matrices to be analyzed in this study do contain a large number of direct overlap spectral interferences for ICP source emission spectrometry. This is because plant tissues, soils, and sewage sludge contain quite high levels of Al, Ca, Fe, K, Na, Mg and other elements that introduce spectral interferences on As, Hg, Sb, Se, Sn, Pb, Tl, and other minor elements.

(3) Interferences are identified for a new sample matrix by aspirating a representative sample and performing 63 2-sec emission integration counts in a scan 1 angstrom on either side of each analyte emission peak centerline. Figure 3 is an example of the plotted spectra for four samples for the Se emission peak. Note the significant Ca interference peak overlap from the sample named "NEWSD2."

Such plots are prepared for all 30 detector channels. The plots are interpreted by comparison to a library of spectrum scan plots performed on known standards. This interpretation information is summarized on a "SPECTRUM SCAN" sheet (Figure 4).

(4) The above procedure was used to identify 88 spectral interferences requiring correction. On-peak interelement correction will be used to remove the effects of these interferences by subtracting a concentration amount from the interfered element detection channel. The amount to be subtracted equals (concentration of interfering element) x correction factor. The correction factors are determined by measuring the false positive reading on the interfered channel when a sample containing 100 ppm interfering element is measured. The correction factor equals the false positive concentration per 1 ppm interfering element. Correction factors are then placed in Group 4 of the appropriate Analytical Control Table (ACT). Correction factors are specific for a given sample matrix and observation position in the inductively coupled plasma.

(5) All analysis data used to generate correction factors and copies of each Group 4 data will be placed in the program "Spectral Interferences" MRI Technical Record Book.

(6) Correction factors will be redetermined each time the ICP torch has been cleaned and reassembled.

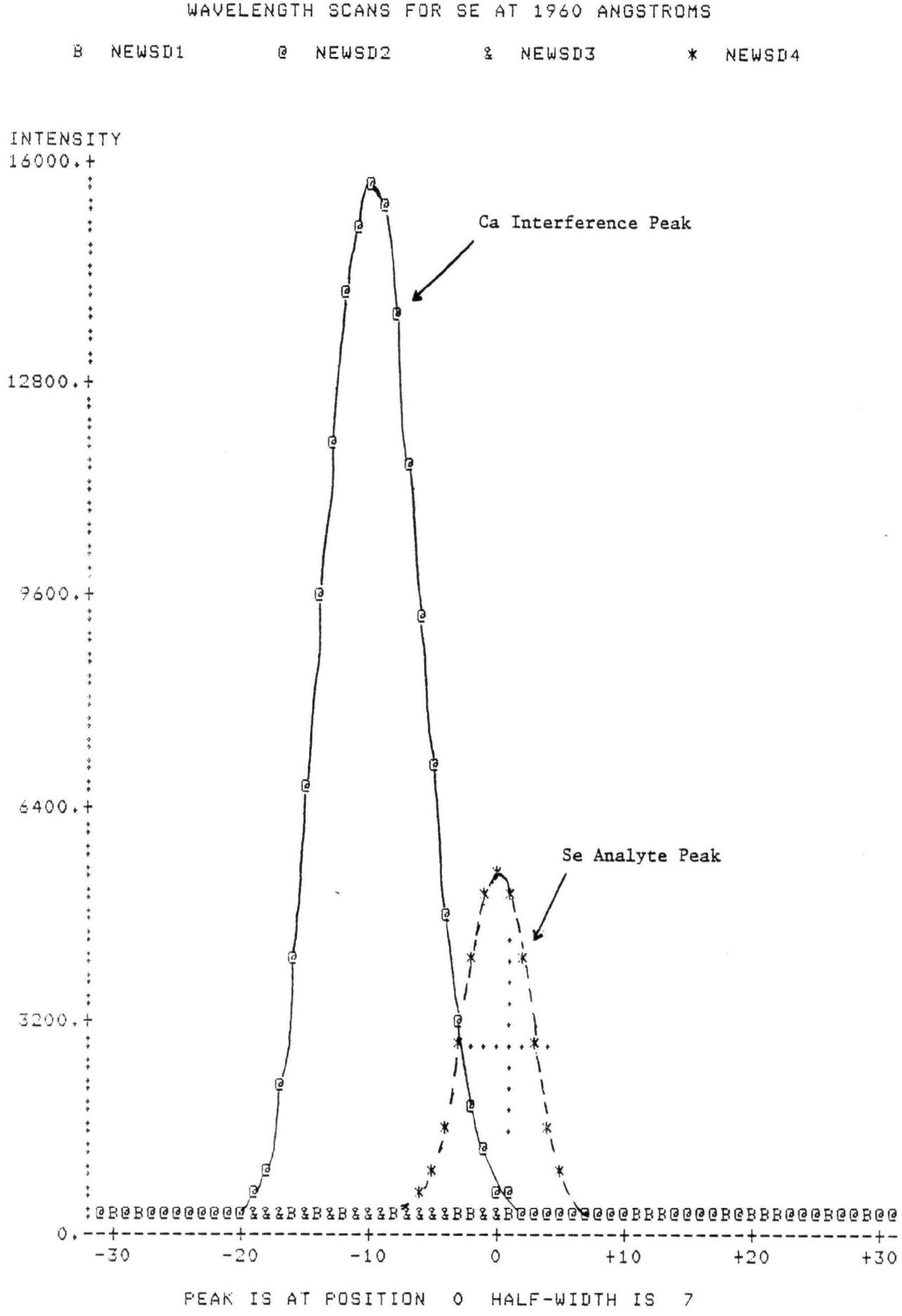
WAVELENGTH SCANS FOR SE AT 1960 ANGSTROMS
B NEWSD1
@ NEWSD2
& NEWSD3
* NEWSD4
INTENSITY
16000.+
12800.+
9600.+
6400.+
3200.+
0.
Ca Interference Peak
Se Analyte Peak
-30
-20
-10
0
+10
+20
+30
PEAK IS AT POSITION 0 HALF-WIDTH IS 7

Figure 3

SPECTRUM SCAN

Project No:_____ Date:_____

Integration Time (sec):_____ Analyst:_____

LCN	Element	Wavelength (A)	Comments
1	LV	1001	
2	Ag	3280	
3	Al	3082	
4	Al	2373	
5	As	1937	
6	B	2496	
7	Ba	4934	
8	Be	2348	
9	Ca	3968	
10	Cd	2288	
11	Co	2286	
12	Cr	2677	
13	Cu	3247	
14	Fe	2599	
15	Fe	2714	
16	Hg	1942	
17	K	7664	
18	Mg	2795	
19	Mn	2576	
20	Mo	2020	
21	Na	5890	
22	Ni	2316	
23	P	2149	
24	Pb	2203	
25	Sb	2068	
26	Se	1960	
27	Sn	1899	
28	Ti	3349	
29	Tl	1908	
30	Y	3710	
31	Zn	2138	

Figure 4

(7) Correction factors will also be redetermined each time repeated analysis of the Interference Check Standard does not give results within ± 1.5 σ of the true values. Table 4 shows the composition of the Interference Check Standard.

TABLE 4

INTERFERENCE CHECK STANDARD[a]

Analyte	(mg/ℓ)	Interferents	(mg/ℓ)
Ag	0.3	Al	120
As	1.0	Ca	600
B	0.5	Fe	500
Ba	0.3	Mg	300
Be	0.1	Na	100
Cd	0.3		
Co	0.3		
Cr	0.3		
Cu	0.3		
Na	0.38		
Mo	0.36		
Ni	0.3		
Pb	1.0		
Sb	1.0		
Se	0.5		
Ti	1.0		
Tl	1.0		
V	0.3		
Zn	10		
K	20		

a Interference QC Sample, EPA-EMSL, Cincinnati, November 1980.

(8) A representative sample from each sample preparation batch will be spectrum scanned, plotted, and evaluated to confirm that all spectral interferences are being compensated by correction factors. This procedure may be discontinued if repeated interference evaluations reveal a constancy of interferences.

b. Accuracy verification of instrument calibration standards

(1) New calibration standards will be prepared every 30 days. See Table 3 for the composition of the mixed calibration standards.

(2) Each of the two types of sample matrices will have a separate set of standards:

Soils and sludges	10% (v/v) HNO_3 (double-distilled)
Vegetables	20% (v/v) HNO_3 (double-distilled)

(3) Each volumetric flask holding the calibration standards will be labeled with the standard name, ACT name, and date.

(4) The accuracy of each new batch of calibration standard will be verified by analyzing a matrix-matched USEPA analytical quality control (AQC) standard. This is done by calibrating the ICP spectrometer with the new standards and analyzing the AQC standard five times: EAANANANANANTDTP. Accuracy is acceptable if all measured values for the AQC standard are within ± 5% of the certified values. If verification is not successful, recalibrate the spectrometer and repeat the test. If verification is still not successful, prepare new standards.

(5) All terminal output for the verification test will be placed in the program "Instrument Calibration" Technical Record Book.

c. Verification of daily instrument calibration

(1) Two quality control standards are to initially verify the accuracy of the initial calibration of the ICP emission spectrometer and to monitor instrument drift. These standards are:

ISC - Instrument Check Standard
Labeled Vnn or Snn for the vegetable or soil matrix, where nn starts at Ø1 and is incremented for each new standare prepared.
STD1 - Calibration reagent blank.

(2) ICSs will be prepared monthly or as needed by the trace metal analysis leader.

(3) The true or accepted concentration values for a new ICS will be determined by first successfully calibrating the ICP spectrometer with existing quality control samples and performing 20 replicate analyses of the new ICS. The mean, standard deviation, and percent relative standard deviation for the replicate analyses will be determined (TDTP).

(4) The true or accepted values for STD1 will be determined the same way.

(5) All computer terminal printouts will be placed in the program "Instrument Calibration" Technical Record Book.

(6) As described in Section 5, "Daily Instrument Calibration Procedure," STD1 and the ICS are analyzed at the beginning and every 10th analysis for a sample set to assure continued acceptable instrument calibration. The control limits are:

STD1 ± 2 standard deviations for mean concentration values
ICS ± 5% from true or accepted concentration values.

(7) Any samples analyzed after the last successful verification of the daily instrument calibration will be reanalyzed after calibration.

d. Verification of purify of double-distilled HNO_3

(1) Each bottle of Merck Suprepur® HNO_3 will be checked for metal contamination before it is used for sample preparation or instrumental analysis.

(2) Each bottle will be dated and marked for "4901A42 Use" when opened.

(3) Each bottle will be kept in a plastic bag when not being used.

(4) The ICP-AES elemental analysis of each bottle will be kept in the program "Instrument Calibration" Technical Record Book.

7. Time/materials requirements: Complete ICP-AES analysis of a given 50-sample batch should require 8 hr labor time. This includes documentation control.

V. Data Analysis, Storage and Retrieval

A. General

1. All data entries will be in accordance with MRI procedure QA-7.

2. All records and data files will be kept in a centralized location in Room 346.

3. All entries of original data or information will be made with waterproof blank ink directly into the appropriate permanent record medium.

4. Entries will be both complete and timely.

5. Calculations and entries of all measured numbers will be according to the following significant figure convention.

B. Significant Figures

All data for this program will be reported with three significant figures.

C. Sample Concentration Calculations

1. The final analyte concentrations will be expressed as micrograms analyte per gram dried sample.

2. The actual calculations to convert ICP emission intensity into a microgram per gram (dry) final analyte concentration will be done immediately upon completion of sample analysis by the computer. The terminal output, following ICP-AES analysis, will be the final concentrations for all channels.

3. The intensity of emission of each analyte element is measured by the spectrometer as a series of emission counts. At the end of the emission intensity measurement period, the count numbers are converted to a digital count and sent to the computer. These counts are compared to linear counts versus concentration relationships whose slope (A0) and intercept (A1) are stored in the Analytical Control Table during instrument calibration:

$$\text{Concentration} = A0 \times \text{emission counts} + A1$$

4. Then, any interelement spectral interference emission is subtracted out:

$$\text{Corrected Concentration} = \text{Uncorrected Concentration} - \sum_{i=1}^{n} K_{1i} C_i$$

where K_{1i} = interelement correction factor, ppm analyte/ppm interferent.

C_i = interferent element concentration, ppm.

5. Lastly, the corrected analyte concentration in micrograms per gram digest is converted to microgram per gram (dry) sample by multiplying the preparation dilution factor:

$$\frac{\mu g \text{ analyte}}{g \text{ digest}} \times \frac{g \text{ digest}}{g \text{ (dry) sample}} = \frac{\mu g \text{ analyte}}{g \text{ (dry) sample)}}$$

6. These final concentrations are also stored on disk.

D. Computer Operating Procedures

1. General hardware/software description

a. The computer system used for this program is a Digital Equipment Corporation PDP 11/23 model with 96K words of dynamic memory and over 5 megabytes of disk storage space. Two terminals are interfaced to the computer: (1) an LA 120 180 character/sec printer terminal, and (2) a VT100 video terminal. The ICP spectrometer is remotely interfaced to the computer by dual 40-port shielded cables.

The LA 120 terminal located beside the ICP emission spectrometer is the console terminal for the computer and is the terminal for operation of the spectrometer. The VT100 terminal, located in Room 342W with the computer, is a remote terminal despite its physical location. One must "log-on" a remote terminal with a proper User Identification Code (UIC) and password.

b. The computer operation system is RSX-11M, which is a real-time multitasking and multiprogramming software system. What this means for our system is that one person can operate the spectrometer at the LA 120 terminal while another person simultaneously runs other programs at the VT100 terminal.

c. The RSX-11M operating system is both powerful and complex. Any questions or problems observed while operating the system should be communicated to the metals analysis task leader.

d. A good overview of RSX-11M is contained in the following two Digital Equipment Coproration Manuals:

(1) Introduction RSX-11M, AA-2555C-TC, Vol. 1A
(2) RSX-11M Beginner's Guide, DEC-11-OMBGAA-D, Vol. 1A

2. ICP-AES analytical quality control software:

a. Two programs have been written to permit immediate quality control evaluation of a sample set analyzed by ICP-AES:

* Generation and storage of accuracy and precision control limits for standard reference mterıals.

* Generation and storage of accuracy and precision control limits for the sample matrix.

* Calculation and storage of detection limıts.

* Testing of all QC samples (SRM, duplicates, and spikes) for accuracy and precision control. All parameters by samples that are out of control are flagged.

* Printout of data summary tables with the correct number of significant figures and flagged for < detection limit results.

* Printout of QC accuracy % recovery summary tables.

* Printout of QC precision relative percent standard deviation summary tables.

b. Table 5 summarizes the analytical quality control statistics and limits used in the two programs.

E. Analytical Data Documentation Control

Below are listed the primary types of data generated during sample preparation and analysis followed by specific means by which it is to be stored:

1. Initial sample preparation sheets: These are to be completed in duplicate by the trace metal analysis leader, who retains one copy. One copy is forwarded for action to the sample preparation analyst.

2. Completed sample preparation sheets: The original SAMPLE PREPARATION SHEET, completed by the sample preparation analyst is placed on the tray with the prepared sample batch. One copy if placed in the current project "Sample Preparation" Technical Record Book (TRB).

3. Spectrum scan plots and summary sheets: The original SPECTRUM SCAN SUMMARY sheet is placed in the project "Spectral Interferences" TRB. A copy of the summary sheet plus the spectrum scan plots are placed in the blue ringed binder marked "Spectral Interferences."

4. Spectral interelement interferences (Group 4): Signed and dated, the terminal output and a hard copy of new Group 4 for either VEG or SOIL ALT is placed in the blue ringed binder marked "SPECTRAL INTERFERENCES."

5. Analyses of the interference check standards: Signed and dated, the terminal output for successful analysis of the Interference Check Standard is placed in the project "Spectral Interferences," TRB.

6. Preparation of interference check standards: All information concerning the preparation and true values of interference check standards will also be placed in the project "Spectral Interferences" TRB.

7. Analyses of USEPA AQC standards: Terminal output for analyses of USEPA Analytical Quality Control Standards for accuracy verification of instrument calibration standards will be placed in the project "Instrument Calibration" TRB.

8. Preparation of USEPA AQC standards: All information concerning preparation and true values for USEPA AQC standards will also be placed in the project "Instrument Calibration" TRB.

TABLE 5

ANALYTICAL QUALITY CONTROL STATISTICS AND LIMITS

1. PRECISION

- CONTROL STATISTIC = S_i = PERCENT RELATIVE STANDARD FOR ith ELEMENT OF DUPLICATED SAMPLES

- CONTROL LIMITS

  WARNING LIMIT = 1.96 S_i (95% CONFIDENCE LEVEL)

  CONTROL LIMIT = 2.58 S_i (99% CONFIDENCE LEVEL)

2. ACCURACY

- CONTROL STATISTIC = P_i = PERCENT RECOVERY OF ith ELEMENT

  SPIKED SAMPLES $$P_i = \frac{100 \times (\text{MEASURED SPIKED SAMPLE CONCENTRATION} - \text{MEASURED UNSPIKED SAMPLE CONCENTRATION})}{\text{SPIKE CONCENTRATION INCREASE}}$$

  REFERENCE SAMPLES $$P_i = \frac{100 \times \text{MEASURED SAMPLE CONCENTRATION}}{\text{KNOWN SAMPLE CONCENTRATION}}$$

- CONTROL LIMITS

  WARNING LIMITS = MEAN $P_i \pm 1.96\ \delta p_i$ (95% CONFIDENCE LEVEL)

  CONTROL LIMITS = MEAN $P_i \pm 2.58\ \delta p_i$ (99% CONFIDENCE LEVEL)

  WHERE δp_i = STANDARD DEVIATION OF MEAN PERCENT RECOVERY OF ith ELEMENT

3. DETECTION LIMITS

- CONTROL STATISTIC = 3 x STANDARD DEVIATION OF 10 OR MORE REPLICATE DETERMINATIONS OF A REPRESENTATIVE SAMPLE

9. Analyses of blank (STD1) and instrument check standard (ICS): The initial analyses terminal output of STD1 and the ICS will be placed in the project "Instrument Calibration" TRB. Subsequent analyses will be part of the analysis sample set data.

10. Preparation of calibration standards and ICS: All information concerning preparation and true values of calibration standards and ICS, will also be placed in the project "Instrument Calibration" TRB.

11. Sample set analyses: The original copy of the "ICP Data Reporting Sheet," will be placed in the project "Sample Analysis" TRB.

A copy of the "ICP Data Reporting Sheet" and all real-time terminal output will be placed in the blue ringed binder marked "Sample Analysis."

The results are also stored on disk under the file specification: DL1:[1,54]digestion code.BRN;1.

12. VREPORT summary of sample set analyses: The VREPORT terminal report of recently completed analyses will be placed with the other terminal output for that sample set in the ringed binder marked "Sample Analysis."

13. ICP-AES analytical quality control software results and reports: The summary tables generated during execution of DOR21.TSK;1 will be forwarded with the appropriate "Sample Analysis" TRB and "Sample Analysis" blue ringed binder for review by the trace metal analysis leader.

Another copy of summary tables plus all terminal output from execution of DOR20.TSK;1 and DOR21.TSK;1 will be placed in the "Sample Analysis" blue ringed binder.

14. Sample analysis data files stored on disk: Each week all new sample analysis data files stored on the current scratch disk in disk drive 1 will be copied onto the backup disk entitled "DA4901."

15. Data reports to the task leader: The analytical summary tables of analysis sample sets approved by the trace metal analysis leader will be forwarded to the task leader with a cover memo.

F. Other Project Documentation Control

1. Purchase requisitions, shipping orders, and memos on stock room purchases will be kept on file by the trace metal analysis leader.

2. Each week all personnel working on the project will submit to the trace metal analysis leader a summary of hours worked.

3. Phone contact reports and other correspondence will be kept on file by the trace metal analysis leader.

VI. Sample Custody and Control

A. Field Samples

1. Samples arriving at MRI from the field will have an MRI "Chain of Custody Record" sheet (Figure 5) with them.

2. The trace metal analysis leader or designee will receive the samples by signing the custody sheet.

3. The sheet will be filed by the trace metal analysis leader in the "Sample Custody" Technical Record Book.

4. Each sample will be logged in the bound "Sample Custody" TRB by completing the following entries:

- Sample Code
- Arrival Date
- Arrival Time
- Signature of Receiver

5. The status of the samples will be updated by completing the following column entries:

- Date
- Digest Code
- Analysis Date
- Report Date
- Comments

6. Samples will be stored on the designated shelves in custody refrigerated storage at all time when not being used for sample preparation.

B. Dried and Prepared Samples

1. Dried or digested sample sets will be stored in a metal cabinet in the Inorganic Analysis Prep Laboratory (Room 344W) until those samples have been analyzed and the data reported.

2. After data reporting, dried and digested samples will be archived in the locked refrigerated sample custody storage.

C. Computerized Sample Status Reporting

1. In addition to the bound primary sample status tracking through the bound MRI "Sample Custody" Technical Record Book, a computerized sample tracking data base will be maintained.

2. This data base file will be an RMS indexed sequential file amenable to DEC DATATRIEVE data base management software.

3. Each sample record will contain the following information:

- Sample Code
- Arrival Date
- Preparation Dae
- Digest Date
- Analysis Date
- Report Date
- Comments Section

4. A weekly status table printout will be presented to the task leader.

5. Appendix B contains a copy of the DATATRIEVE file information.

VII. Safety

All samples and extracts will be considered hazardous and will be handled with utmost care. Rigid sample and extract control will be exercised to ensure sample integrity and minimize human exposure.

All pertinent regulations of the MRI Safety and Health Manual and the MRI General Safety Regulations for the Use of Carcinogenic Materials will be followed. In particular, all equipment and containers will be decontaminated as prescribed.

VIII. References

1. Page, A. L., and A. C. Chang, "Trace Elements Impact on Plants During Cropland Disposal of Sewage Sludge," In: National Conference on Acceptable Sludge Disposal Technology [Proceedings, 5th], 1978, pp. 91-6.

2. Page, A., "Sludge Treatment and Disposal," Vol. 2, USEPA Transfer Technology, EPA-625/14-78-012, October 1978.

3. Naylor, L., and R. Loehr, "Increase in Dietary Cadmium as a Result of Application of Sewage Sludge to Agricultural Land," Environ. Sci. and Technol., 15, 881-6 (1981).

4. Stoewsand, G., "Trace Metal Problems with Industrial Waste Materials Applied to Vegetable Producing Soils," In: The Safety of Foods, 2nd Edition, H. D. Graham (ed.), Avi Publishing, Westport, Connecticut, 1980, pp. 423-43.

5. Garcia, W., et al., "Metal Accumulation and Crop Yield for a Variety of Edible Crops Grown in Diverse Soil Media Amended with Sewage Sludge," Environ. Sci. and Technol., 15, 793-804 (1981).

6. Swanson, S., "Summary of Analytical Methods, Quality Assurance Procedures, and Analytical Results for Priority Pollutants," Draft Final Report, POTW Sludge Analysis--Task 35, EPA Contract Nos. 68-03-2565 and 68-02-5915, Midwest Research Institute, Kansas City, Missour, 1981.

APPENDIX A

EPA INTERIM METHOD 200.7

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

METHOD 200.7

INTERIM

U. S. ENVIRONMENTAL PROTECTION AGENCY
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

Foreword

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory - Cincinnati, with the cooperation of the EPA-ICP Users Group. Their cooperation and support is gratefully acknowledged.

This method represents the current state-of-the-art, but as time progresses, improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account. This is especially true when dissolved solids exceed 1500 mg/l. (See 4.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See 4.)

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

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

Table 1 - Recommended Wavelengths[1] and Estimated Instrumental Detection Limits

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

(1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 4.1.1).

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

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

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 lines 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 4.1 (and tests for their presence as described in 4.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 Dissolved -- Those elements which will pass through a 0.45 um membrane filter.

3.2 Suspended -- Those elements which are retained by a 0.45 um membrane filter.

3.3 Total -- The concentration determined on an unfiltered sample following vigorous digestion (Section 8.3), or the sum of the dissolved plus suspended concentrations. (Section 8.1 plus 8.2).

3.4 Total recoverable -- The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 8.4).

3.5 Instrumental detection limit -- The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 Sensitivity -- The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 Instrument check standard -- A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 6.6.1)

3.8 Interference check sample - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 6.6.2.)

3.9 Quality control sample -- A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 6.6.3)

3.10 Calibration standards -- a series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 6.4)

3.11 Linear dynamic range -- The concentration range over which the analytical curve remains linear.

3.12 Reagent blank -- A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 6.5.2)

3.13 Calibration blank -- A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 6.5.1)

3.14 Method of standard addition -- The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 9.6.1.)

4. Interferences

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

4.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selec-

tion of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

The interference information, which was collected at the Ames Laboratory[1], is expressed as analyte concentration eqivalents (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 2,

[1] Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011

Table 2. Analyte Concentration Equivalents (mg/l) Arising From Interferents at the 100 mg/l Level

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

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 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

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

4.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of

interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aersol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

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

4.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 4.2.1 through 4.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of

Table 3. Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2.

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

Interferents	(mg/l)
Al	1000
Ca	1000
Cr	200
Cu	200
Fe	1000
Mg	1000
Mn	200
Ni	200
Ti	200
V	200

the analyte elements thereby distorting the accuracy of the reported values.

4.2.1 Serial dilution--If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit (13.3) that has been established for that matrix.). If not, a chemical or physical interference effect should be suspected.

4.2.2 Spike addition--The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See 4.2.3).

4.2.3 Comparison with alternate method of analysis--When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

4.2.4 Wavelength scanning of analyte line region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

5. Apparatus

5.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radiofrequency generator.

5.1.3 Argon gas supply, welding grade or better.

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

6. Reagents and standards

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

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

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

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

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

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

6.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (13.6).

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

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow:

6.3.1 Aluminum solution, stock, 1 ml = 100 µg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 ml of (1+1) HCl and 1 ml of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask add an additional 10 ml of (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.2 Antimony solution stock, 1 ml = 100 µg Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water,

add 10 ml (1+1) HCl and dilute to 1000 ml with deionized, distilled water.

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

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

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

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

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

6.3.8 Calcium solution, stock, 1 ml = 100 µg Ca: Suspend 0.2498 g

$CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

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

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

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

6.3.12 Iron solution, stock, 1 ml = 100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

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

6.3.14 Magnesium solution, stock, 1 ml = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0

ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

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

6.3.16 Molybdenum solution, stock, 1 ml = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 ml.

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

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

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

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

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

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

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

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

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

6.4 Mixed calibration standard solutions--Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 6.4.1 thru 6.4.5) Add 2 ml of (1+1) HNO_3 and 10 ml of (1+1) HCl and dilute to 100 ml with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or

unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 6.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

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

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

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

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

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

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 ml of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 ml with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/l. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

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

6.5.1 The calibration blank is prepared by diluting 2 ml of (1+1) HNO_3 and 10 ml of (1+1) HCl to 100 ml with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

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

6.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

6.6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 11.1.1.)

6.6.2 The interference check sample is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest but known concentration of interfering elements that will

provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/l or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 11.1.2).

6.6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/l and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 11.1.3.)

7. Sample handling and preservation

7.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample 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) by depleting concen-

trations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polyproplyene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

7.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

7.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-um membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 ml of (1+1) acid per liter should be sufficient to preserve the sample.

7.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-um membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

7.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

8. Sample Preparation

8.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by

heat as described in 8.3.

8.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-ml Griffin beaker and add 4 ml conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 ml), cool, add 10 ml HCl (1+1) and 15 ml deionized, distilled water per 100 ml dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

NOTE 4: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

8.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See

Note 5.) Add 3 ml of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 ml portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 ml of 1+1 HCl and 15 ml of deionized, distilled water per 100 ml of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

NOTE 5: If low determinations of boron are critical, quartz glassware should be used.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in 8.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

8.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 ml of (1+1) HNO_3 and 10 ml of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 ml making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 ml and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

9. Procedure

9.1 Set up instrument with proper operating parameters established in Section 5.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

9.2 Initiate appropriate operating configuration of computer.

9.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 6.4. Flush the system with the calibration blank (6.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 µg/l extended flush times of 1 to 2 minutes may be required.

9.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

9.5 Begin the sample run flushing the system with the calibration blank solution (6.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (6.6.1) and the calibration blank (6.5.1) each 10 samples.

9.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

9.6.1 The standard addition technique (13.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of

A and B are measured and corrected for nonanalyte signals signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

For the results from this technique to be valid, the following limitations must be taken into consideration:

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

10. Calculation

10.1 Reagent blanks (6.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

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

10.3 Data should be rounded to the thousandth place and all results should be reported in mg/l up to three significant figures.

11. Quality Control (Instrumental)

11.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

11.1.1 Analyze an appropriate instrument check standard (6.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ± 5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (6.5.1) at a frequency of 10%. The result should be within the established control limits of 2 standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

11.1.2 To verify interelement and background correction factors analyze the interference check sample (6.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control

limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

11.1.3 A quality control sample (6.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within ± 5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

12. Precision and Accuracy

12.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

13. References

13.1 Winge, R.K., V.J. Peterson, and V.A. Fassel, "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines, EPA-600/4-79-017.

13.2 Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements," Chemical Analysis, Vol. 46, pp. 41-42.

13.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

Table 4. ICP Precision and Accuracy Data

Element	Sample # 1 True Value µg/l	Sample # 1 Mean Reported Value µg/l	Sample # 1 Mean Percent RSD	Sample #2 True Value µg/l	Sample #2 Mean Reported Value µg/l	Sample #2 Mean Percent RSD	Sample #3 True Value µg/l	Sample #3 Mean Reported Value ug/l	Sample #3 Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

13.4 Garbarino, J.R. and Taylor, H.E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy 33, No. 3(1979).

13.5 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

13.6 Annual Book of ASTM Standards, Part 31.

APPENDIX B

DATATRIEVE FILE STRUCTURE FOR THE 4901A42 SAMPLE STATUS DATA BASE FILE

:REPORT 12

STATUS REPORT OF MRI PROJECT 4901A-42 METALS ANALYSES 19-MAY-82
PAGE 1

SAMPLE	ARRIVAL DATE	PREP DATE	DIGEST CODE	ANALYSIS DATE	REPORT DATE	COMMENTS
1012	05-03-82					
1022	05-03-82					
1032	05-03-82					
1042	05-03-82					
1052	05-03-82					
1035	05-03-82					
1017	05-03-82					
1027	05-03-82					
1062	05-03-82					
1072	05-03-82					
1082	05-03-82					
1067	05-03-82					
1077	05-03-82					
1087	05-03-82					
1037	05-03-82					
1047	05-03-82					

DTR

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DOMAIN TASK42
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DTR



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 03 ARRIVAL-DATE PIC X(8).
 03 PREP-DATE PIC X(8).
 03 DIGEST-CODE PIC X(4).
 03 ANALYSIS-DATE PIC X(8).
 03 REPORT-DATE PIC X(8).
 03 COMMENTS PIC X(30).
;
DTR



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SET COLUMNS-PAGE=80
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REPORT END;
END-PROCEDURE
DTR
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