INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRIC METHOD FOR THE DETERMINATION OF DISSOLVED TRACE ELEMENTS IN NATURAL WATER

U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS

Multiply	By	To obtain
Volume		
milliliter (mL)	0.03382	ounces, fluid
liter (L)	0.2642	gallon
Mass		
picogram (pg)	0.00000000003527	ounce, avoirdupois
microgram (µg)	0.00000003527	ounce, avoirdupois
milligram (mg)	0.00003527	ounce, avoirdupois
gram (g)	0.03527	ounce, avoirdupois

The following abbreviations were also used in this report:

Unit	Abbreviation
Concentration	
milligram per liter	mg/L
microgram per liter	µg/L
Distance	
millimeters	mm
Flow	
Liters per minute	L/min
Power	
kilowatts	kW
Pressure	
pounds per square inch	psi
Intensity	
Counts per second	cps
Time	
seconds	s
milliseconds	ms

Inductively Coupled Plasma-Mass Spectrometric Method for the Determination of Dissolved Trace Elements in Natural Water

By *J.R. Garbarino and H.E. Taylor*

ABSTRACT

An inductively coupled plasma-mass spectrometry method was developed for the determination of dissolved Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sr, Tl, U, V, and Zn in natural waters. Detection limits are generally in the 50-100 picogram per milliliter (pg/mL) range, with the exception of As which is in the 1 microgram per liter (µg/L) range. Interferences associated with spectral overlap from concomitant isotopes or molecular ions and sample matrix composition have been identified. Procedures for interference correction and reduction related to isotope selection, instrumental operating conditions, and mathematical data processing techniques are described. Internal standards are used to minimize instrumental drift. The average analytical precision attainable for 5 times the detection limit is about 16 percent. The accuracy of the method was tested using a series of U.S. Geological Survey Standard Reference Water Standards (SWRS), National Research Council Canada Riverine Water Standard, and National Institute of Standards and Technology (NIST) Trace Elements in Water Standards. Average accuracies range from 90 to 110 percent of the published mean values.

INTRODUCTION

Inductively coupled plasma-mass spectrometry (ICP-MS) combines the ionization efficiency of the argon plasma with the sensitivity and selectivity of mass spectrometric separation. Greater than 80 percent of the elements have primary ionization potentials that are attainable using an argon plasma as the ionization source; therefore, absolute detection limits are consistently in the 0.1 µg/L range.

Analyte ions produced in the plasma are sampled at the instrument-plasma interface through concentric orifices in a pair of nickel sampling cones. Electrostatic lenses accelerate and focus the ion beam into the quadrupole mass analyzer. By applying a pair of radio frequencies and direct-current potentials to the quadrupole rods, only ions with a specific mass-to-charge ratio (m/z) are transmitted to the detector; ions with other m/z ratios collide with the rods and are lost. The ions impinge on a Channeltron-type detector where a current pulse is generated and counted. The detector is mounted 90 degrees off-axis to minimize background signal contributions from photons emitted by the plasma. Inherent to the technique is the capability of selectively measuring all isotopes of a given element, thereby providing isotopic ratio information and allowing isotope dilution analysis to be performed.

Spectral interferences result in the analysis of an element primarily from spectral overlap of isotopes from other elements or molecular ion species that cannot be resolved from the analyte ion. Concurrent elemental isotopic interferences may be eliminated or reduced by a chemical separation to remove the interfering element, by mathematical correction, or by selection of an alternative isotope, whenever possible. In this case of direct spectral overlap from a concomitant ion, use of a different analytical isotope is the best alternative for eliminating interferences. When the analyte is monoisotopic, chemical separation or mathematical correction are the only alternatives.

Spectral interferences attributable to molecular ions, for example, $^{43}Ca^{16}O^+$ interference on $^{59}Co^+$, require a combination of compensation procedures for elimination of interference. First, the degree of oxide formation is directly affected by the operating conditions associated with the introduction of aqueous sample aerosol. Oxide formation can be reduced by optimizing nebulizer argon flow rates, by applying solvent desolvation techniques to reduce water entering the plasma, or by the addition of small quantities of nitrogen to the argon gas stream. When determining analyte concentrations in the µg/L range, an additional mathematical correction may be required by calibrating the apparent analyte concentration as a function of oxide interferent. Molecular ion interferences associated with other combinations of elements, for example, $^{35}Cl^{16}O^+$ interference on ^{51}V, can either be eliminated through the chemical separation of chloride in the sample or through mathematical corrections based on natural isotopic abundances. These mathematical corrections are only accurate to 10-20 percent.

Spectral interferences from multiple charged ions are not generally found. Most elements have second ionization potentials greater than what is attainable through plasma ionization (that is, greater than 16 electron volts).

Sample matrix composition affects the magnitude of analyte signals. Analyte signal intensities are suppressed with increasing concentration of many matrix elements. Generally, lighter mass analytes are subject to greater suppressions than heavier mass analytes, and heavier matrix elements cause more severe suppression effects. These suppression effects are thought to result from changes in ion transmission through the ion optics preceding the mass analyzer (Gillson and others, 1988). Suppression effects can be reduced by adjusting the potentials applied to the electrostatic lenses, by altering the matrix through chemical separations, or by modifying the sample-introduction procedure. Compensation for signal suppressions using standard additions, isotope dilution analysis, or internal standards is also effective. However, due to the mass relationship of the suppression phenomena, multiple internal standard elements are required to span the entire mass range.

The purpose of this report is to describe methodology using a Perkin Elmer-Sciex, Model 250, modified inductively coupled plasma-mass spectrometer for the simultaneous determination of dissolved trace metals in natural water, including Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sr, Tl, U, V, and Zn.

Gratitude is expressed to the following coworkers for their suggestions and assistance in performing this research and development work: R.C. Antweiler, T.I. Brinton, D.B. Peart, and D.A. Roth.

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRIC METHOD

Application of method

This ICP-MS method is used for the determination of dissolved-constituents in water having dissolved solids concentrations of less than 0.5 percent, by weight; appropriate dilution is required for samples with greater than 0.5 percent solids. Water samples must be filtered through a 0.4 micrometers (µm) membrane filter (particle-size limit for dissolved constituent definition in most water quality studies is 0.45 µm, Hem, 1985) and acidified with ultrapure nitric acid to pH less than 2. Table 1 specifies detection limits and lower limits of quantitation for analytes included in this method; the calibration limit for all elements is 500 µg/L. Samples having analyte concentrations exceeding the calibration range must be diluted and re-analyzed. The calibration range for each analyte was selected using the concentration range of the analyte normally present in natural water as a guide. This concentration range may be adjusted by using an alternate isotope having a lower natural abundance or by increasing the concentration of the upper calibration standard. However, if an alternate isotope is used, evaluation of isobaric or polyatomic ion interferences must be determined. The upper calibration concentration can be increased to a maximum limit of about 1 mg/L depending on the natural abundance of the isotope. However, concentrations greater than this limit can exceed the detector response of 1.5 million counts per second (cps). In addition, an offset potential may be applied to the entrance rods of the quadrupole (OminRange mode) for a specific isotope to extend the 1 mg/L limit. When a rod-offset potential is used for an isotope, any corrections on that isotope based on natural abundance ratios may become inaccurate.

Summary of Method

All the analytes are determined sequentially according to mass, on a single aliquot utilizing argon plasma ionization, mass spectrometric separation, and electron mulitplier detection. Instrumental operating parameters are listed in table 2. The "parameter set" used for data acquisition is shown in table 3. Each analysis is based on the mean of five replicate determinations. Calibration is performed using a reagent blank and three multielement calibration standards. Linear regression analysis, through zero and based on three points, is used to generate the calibration equation. All standards and samples are blank subtracted to insure correction for contamination as well as background correction.

Interferences

Isotopes used in this method were chosen on the basis of a compromise between the magnitude of their natural abundance and freedom from isobaric and polyatomic ion interferences. However, in the cases of ^{51}V, ^{60}Ni, and ^{75}As, interferences from polyatomic species can not be avoided and therefore require mathematical correction. Corrections on ^{51}V and ^{75}As are automatically calculated in real time by the Elan data-processing software using equations 1 and 2 below. Vanadium-51 intensity is affected by the presence of chloride in the sample matrix. The interfering molecular ion formed is $^{35}Cl^{16}O$. The contribution of $^{35}Cl^{16}O$ to the signal is determined by measuring the ion intensity at mass-to-charge ratio (m/z) 53 and subtracting the contribution from chromium, resulting in a net vanadium intensity ($^{51}V_{corr}$). Terms in bold are calculated from isotopic natural abundances.

Elemental equation 1:

$$^{51}V_{corr} = {}^{51}V - 3.065(^{53}Cr) + 0.3494(^{52}Cr)$$

as derived from:

$$^{51}V_{corr} = {}^{51}V - \mathbf{[^{35}Cl^{16}O / ^{37}Cl^{16}O]} \times \{ ^{37}Cl^{16}O - \mathbf{[^{53}Cr / ^{52}Cr]} \times {}^{52}Cr\} \qquad (1)$$

A similar process is used for the ArCl interference on arsenic-75, resulting in a net arsenic ($^{75}\mathrm{As}_{\mathrm{corr}}$).

Elemental equation 2:

$$^{75}\mathrm{As}_{\mathrm{corr}} = {}^{75}\mathrm{As} - 3.065({}^{77}\mathrm{Se}) + 0.2600({}^{82}\mathrm{Se})$$

as derived from:

$$^{75}\mathrm{As}_{\mathrm{corr}} = {}^{75}\mathrm{As} - [\mathbf{{}^{40}Ar^{35}Cl / {}^{40}Ar^{37}Cl}] \times \{ {}^{40}\mathrm{Ar}^{37}\mathrm{Cl} - [\mathbf{{}^{77}Se / {}^{82}Se}] \times {}^{82}\mathrm{Se}\} \quad (2)$$

The corrections made to $^{59}\mathrm{Co}$ and $^{60}\mathrm{Ni}$ are provided by a data-processing software program executed following the analyses. Interferences on cobalt-59 and nickel-60 arise from the formation of $^{43}\mathrm{Ca}^{16}\mathrm{O}$, $^{42}\mathrm{Ca}^{16}\mathrm{OH}$, and $^{43}\mathrm{Ca}^{16}\mathrm{OH}$. A set of equations describing the apparent analyte concentration as a function of the calcium concentration are generated by the program. Knowing the calcium concentration in the sample allows calculation of the apparent concentration and subtraction of its contribution from the result. The general form of the equations are listed below for cobalt-59 and nickel-60.

$$^{59}\mathrm{Co}_{\mathrm{corr}} = {}^{59}\mathrm{Co}_{\mathrm{uncorr}} - {}^{59}\mathrm{Co}_{\mathrm{A,}} \quad (3)$$

where

$$^{59}\mathrm{Co}_{\mathrm{A}} = \mathrm{Ca} \times ({}^{59}\mathrm{Co} / \mathrm{Ca}) + b$$

$$^{60}\mathrm{Ni}_{\mathrm{corr}} = {}^{60}\mathrm{Ni}_{\mathrm{uncorr}} - {}^{60}\mathrm{Ni}_{\mathrm{A,}} \quad (4)$$

where

$$^{60}\mathrm{Ni}_{\mathrm{A}} = \mathrm{Ca} \times ({}^{60}\mathrm{Ni} / \mathrm{Ca}) + b$$

Terms having subscripts corr, uncorr, and A represent corrected, uncorrected, and apparent isotope intensities, the terms in parentheses represent slope values of apparent analyte intensity as a function of the Ca concentration, and b is the corresponding intercept term.

Chromium-52 and manganese-55 (table 4) have interferences associated with the argon plasma and aqueous aerosol. Correction for these molecular ions in the plasma and aerosol can be accomplished through blank subtraction.

Table 4 lists the polyatomic interferent, the correction method, the interferent concentration range for which the correction is suitable, and the expected accuracy of the correction in this range. Other possible interferences are listed in table 5. These interferences are normally not in the analysis of natural waters; therefore, corrections are not routinely performed. However, the analyst must be aware that there could be interferences and be knowledgeable of the sample-matrix composition. Ideally, a semiquantitative scan of the entire elemental mass range should be completed to identify any interfering species.

Samples with total dissolved solids greater than 0.5 weight percent must be diluted prior to analysis. Total dissolved solids of greater than 0.5 percent affect both physical and chemical interferences.

Internal standards are used to minimize instrumental drift and ionization suppression effects. Three internal standard elements are used for separate mass regions. These are Rh, Pr, and Bi; see table 6 for the concentrations and masses referenced to each internal standard. The analyst must confirm that these internal standard elements are not present naturally in the sample matrix. The internal standards are introduced into the sample stream to the nebulizer using the manifold shown in figure 1. A surfactant (Brij 35, see table 6) is introduced with the internal standards to insure smooth flow characteristics. Air is introduced in combination with a glass mixing coil for thorough mixing. A debubbler is used to remove the air segments prior to introducing the sample to the nebulizer. A Babington-type nebulizer is required to eliminate total or partial nebulizer constrictions, which would alter nebulizer efficiency.

ANALYTICAL PROCEDURE FOR THE DETERMINATION OF TRACE ELEMENTS IN WATER

Calibration and Sample Analysis

Verification that the nebulizer is operating properly is made visually by checking the aerosol production, operating pressure, and mass-flow controller reading prior to igniting the plasma. If the torch has been repositioned for any reason the torch-box position must be re-optimized using the vertical and horizontal adjustments while monitoring the signal from 100 μg/L ^{63}Cu through <Applications> <Graphics> pathway (<> denote computer software modules) and the *scan* “parameter set” (see Appendix 3).

The Elan instrumentation must warm-up for 1 hour prior to calibration. The ion optics must be adjusted prior to instrument calibration. These adjustments are made from the <Applications> <Graphics> pathway and the “setup parameter set” while aspirating 100 μg/L solution of Li, Rh, and Pb. The signal response for Rh is maximized while maximizing and equating the signal response for Li and Pb. Generally, adjustments of ± 1 to 5 units to the plate (P, nominally 15) and/or stop (S2, nominally 20) lens potentiometers is sufficient under usual instrumental conditions. Normally, the ion intensity for Rh will be 100,000 to 200,000 cps with Li and Pb ion intensities of 20,000 to 40,000 cps, with surfactants and somewhat lower without. If Rh, Li, and Pb intensities do not fall within these ranges or lens adjustment cannot equalize Li and Pb, then the following should be checked: (1) Ion lens settings; (2) mass calibration; (3) physical condition of the sampler and skimmer cones (salt buildup around orifices affect ion transmission efficiency); and (4) nebulizer performance.

Calibration is performed through the analysis of multiple element standard solutions within a set of unknown and reference samples from the <Applications> <Quant Analysis> path and “qa parameter set”. Select a unique dataset, calibration, and report name. While constructing your dataset use 'template' dataset as a guide. The calibration file must generate equations based on a linear regression through zero. Reference standards should be analyzed after every 6 to 8 samples. Include the calcium standards identified as 'CA50' and 'CA100' at the end of the sample set. These two standards represent calcium concentrations of 50 and 100 μg/mL, respectively, and are used to generate interference corrections for Co and Ni. Load samples into the sampler and switch to the "automatic" mode to start the analyses.

Reports are stored in the file specified in summary format and identified by the .PRN extension in the filename. Summary format includes intensity ratios as well as concentration results.

Processing analytical data

The data received from the Elan software is processed by a Fortran program ICPMS.EXE that corrects for interferences on Co and Ni , checks for values outside the calibration range, truncates data at the detection limits, and reformats data. ICPMS.EXE is in the reports directory on the ICP-MS IBM computer. Execute the program by by entering <ICPMS>. The following inputs are required during the program execution (program queries are in italics; analyst responses are in bold type):

```
Enter ICP-MS data file name - filename.prn
```

```
....... Processing-BLANK
```

Program processes each sample analyzed.

```
...Sample calcium concentration in PPM...

Enter Ca conc in sample 1789:  117.6
```

An entry will be required for each sample. Therefore Ca data must be available before this program is executed. Calcium results are required for each sample.

```
....... Making print file filename.TXTt
```

Generates an ASCII file of concentration results that may be printed from a word processor software package.

```
....... Making ms file = filename.MS
```

This generates a file for the Apollo workstation database.

```
....... Making qcm file = filename.QCM
```

This generates a file for the Apollo QC samples database.

In addition, a fourth file is generated to archive the pertinent data from the filename.prn file.

Accuracy and Precision

The accuracy of the method was tested using a series of U.S. Geological Survey Standard Reference Water Samples (SRWS), National Institute of Standards and Technology (NIST), and National Research Council Canada (SLRS-1) reference water standards. Linear regression analysis of the experimental published values for most analytes are shown in figures 2-18. Analytes that were not certified in all the reference standards were not included. However, boron and uranium were certified in at least one reference standard. Analysis of NIST 1643b gave 110 µg/L as compared to a certified mean value of 96 µg/L for boron. Analysis of SLRS-1 gave 0.33 µg/L as compared to a certified mean of 0.28 µg/L for uranium. The linear regression statistics for experimental versus published values corresponding to figures 2-18 are listed in table 7. The accuracy is generally within 90-110 percent of the published mean values. The analytical precisions that can be expected at 5 times the detection limit, 10 µg/L, and 100 µg/L are compiled in table 8. The mean precision of all the isotopes at the quantitation limit is about 16 percent.

Quality control consisted of analyzing a known reference standard after every six unknown samples. Reference standards routinely used are SWRS, NIST, and SLRS-1 standards, alone or in combination. A control level is based on 1.5 to 2.0 standard deviations of the most probable mean value provided in the standard certification. When results do not satisfy the control, the samples preceding the last reference standard are re-analyzed or, in the case of uniform instrumental drift, mathematically adjusted.

SUMMARY

This report provides a detailed method for the simultanteous determination of variety of dissolved trace elements in natural waters including Al, As, B, Ba, Be, Cd, Co, Cr, Li, Mn, Mo, Ni, Pb, Sr, Tl, U, V and Zn. Detection limits in the 50 to 100 nanogram per liter range (As is 0.6 µg/L) are easily obtained in the multielement mode. Several of the more important interelement interferences are corrected mathematically. Measurement precision is generally better than 20 percent relative standard deviation with an accuracy of about ±10 percent of the amount present.

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Table 1. Detection and quantitation limits, in micrograms per liter, for inductively coupled plasma-mass spectrometry using internal standard manifold injection

[The calibration limit[1] for all elements is 500 micrograms per liter]

Element[2]	Detection limit[3]	Quantitation limit[4]
^{7}Li	0.03	0.06
^{9}Be	0.02	0.08
^{11}B	0.4	2.4
^{27}Al	0.2	0.42
^{52}Cr	0.2	0.54
^{51}V	0.08	0.28
^{55}Mn	0.06	0.23
^{59}Co	0.008	0.03
^{60}Ni	0.03	0.16
^{63}Cu	0.02	0.1
^{66}Zn	0.08	0.39
^{75}As	0.6	2.4
^{88}Sr	0.01	0.08
^{95}Mo	0.09	0.22
^{111}Cd	0.1	0.46
^{137}Ba	0.1	0.34
^{205}Tl	0.05	0.14
^{208}Pb	0.06	0.29
^{238}U	0.06	0.26

[1] Limit using injection method calibration scheme; linear range extends to approximately 1 mg/L.

[2]. Elements listed show specific isotope used for measurement.

[3] Detection limit at the 99 percent confidence level calculated following the method of Skogerboe and Grant (1970).

[4] Quantitation limit, the experimentally determined analyte concentration that can be reported with 99 percent confidence. Calculated as QL = t X s, where t is the student t statistic at 99 percent confidence level and s is the standard deviation of the analyses of a synthetic standard at a concentration of 5 times the detection limit for the respective analyte.

Table 2: Instrumental operating parameters and accesssory specifications for inductively coupled plasma-mass spectrometry determination of trace metals in natural waters

[MFC, mass-flow controller; %, percent]

Parameter	Instrument setting
	Inductively coupled plasma
Plasma gas	13 liters per minute; 68% full scale MFC
Auxiliary gas	1 liter per minute; 69% full scale MFC
Nebulizer gas	0.5 liter per minute; 59-60% full scale MFC depending on type of nebulizer
Incident power	1.2 kilowatts
Reflected power	Minimized
Sampling zone	10 millimeters from initial radiation zone as determined using the red bullet-shaped yttrium atomic-emission as a point of reference. (Note point of reference affected by incident power and nebulizer flowrate.)
Torch	Extended torch design or standard PlasmaTherm torch.
	Sample introduction
Babington-type nebulizer	Operating pressure 36-38 pounds per square inch
Pump	Gildon Minipuls II, peristaltic
Manifold for internal standard introduction	See figure 2
Autosampler	Wash cycle of 100 seconds Delay cycle of 50 seconds
	Quadrupole
Parameter set	QA
Rod offset volts	0.0
Electrostatic lens	Nominal potentiometer units
Barrel (B)	64
Einzel (E1)	95
Plate (P)	15 ± 5
Stop (S2)	20 ± 5

Table 3: Quality assurance parameter set for inductively coupled plasma-mass spectrometry quantitative analysis

[from Elan software; Parameter entry using file 'qa'; ms, millisecond, Time factor = 1 and Omni range = 0.0 for all elements]

For time factor =	1	Estimated times	(minutes:seconds)
Replicate time (ms)	400	Replicate	0:10
Dwell time (ms)	50	Sample	0:50
Sweeps/replicate	8	Resolution	Normal
Number of replicates	5	Calculation freq.	
Points across peak	1	Polarity	Positive

Element	Isotope mass	Correction programmed
Li	7	None
Be	9	None
B	11	None
Al	27	None
V	51	Cr
Cr	52	None
Mn	55	None
Co	59	None
Ni	60	None
Cu	63	None
Zn	66	None
Sr	88	None
Mo	95	None
Cd	111	None
Rh	103	None
Ba	137	None
Pr	141	None
Tl	203	None
Pb	208	None
U	238	None
Bi	209	None

Table 4: Interelement interference corrections for inductively coupled plasma-mass spectrometry method

[µg/ml, microgram per milliliter; %, percent]

Elements	Interferences	Equation	Range	Accuracy
^{51}V	$^{35}Cl^{16}O$	1	0-250 µg/mL Cl	5 to 10%
^{59}Co	$^{43}Ca^{16}O$, $^{42}Ca^{16}OH$	3	0-250 µg/mL Ca	-2 to 6%
^{60}Ni	$^{44}Ca^{16}O$	4	0-250 µg/mL Ca	-5 to 1.4%
^{75}As	$^{40}Ar^{35}Cl$	2	0-250 µg/mL Cl	-1 to 8%
Interferences corrected through blank subtraction				
^{52}Cr	$^{40}Ar^{12}C, ^{36}Ar^{16}O$			
^{55}Mn	$^{40}Ar^{14}NH$			
^{78}Se	$^{38\,40}Ar_2$			

1 $^{51}V_{corr} = {}^{51}V - [\mathbf{^{35}Cl^{16}O / {}^{37}Cl^{16}O}] \times \{ ^{37}Cl^{16}O - [\mathbf{^{53}Cr / {}^{52}Cr}] \times {}^{52}Cr\}$

2 $^{75}As_{corr} = {}^{75}As - [\mathbf{^{40}Ar^{35}Cl / {}^{40}Ar^{37}Cl}] \times \{ ^{40}Ar^{37}Cl - [\mathbf{^{77}Se / {}^{82}Se}] \times {}^{82}Se\}$

3 $^{59}Co_{corr} = {}^{59}Co_{uncorr} - {}^{59}Co_{A}$

4 $^{60}Ni_{corr} = {}^{60}Ni_{uncorr} - {}^{60}Ni_{A}$

Table 5: **Potential interferences that could affect accuracy for selected elements in inductively coupled plasma-mass spectrometry**

Element	Interferent
^{7}Li	none
^{9}Be	none
^{11}B	none
^{27}Al	^{26}MgH
^{60}Ni	$^{28}Si^{16}O_2$
^{63}Cu	$^{47}Ti^{16}O^{23}$, $Na^{40}Ar$
^{66}Zn	$^{50}Ti^{16}O$, $^{50}V^{16}O$, $^{50}Cr^{16}O$, $^{34}S^{16}O_2$, $^{33}S_2$, $^{26}Mg^{40}Ar$
^{88}Sr	$^{40}Ca^{48}Ca$
^{95}Mo	^{94}ZrH, ^{94}MoH, $^{23}Na^{35}Cl^{37}Cl$
^{111}Cd	$^{95}Mo^{16}O$
^{137}Ba	none
^{205}Tl	none
^{208}Pb	none
^{238}U	none
^{103}Rh	$^{86}Sr^{16}OH$, $^{87}Sr^{16}O$
^{141}Pr	none
^{209}Bi	none

Table 6: Calibration concentrations of multielement standards in micrograms per liter for inductively coupled plasma-mass spectrometry

[%, percent, mL, milliliter, µg/L, micrograms per liter, w/v, weight volume]

Standard	Concentration
BLNK[1]	0.0
STD1A[2]	10.0
STD2A[3]	100.0
STD3A[4]	500.0

1 1% HNO_3 [1/100] in deionized water

2 10:100 dilution of standard STD2A or STD2B + 1 mL HNO3

3 1:100 dilution of stock Mix A or B + 1 mL HNO_3

4 5:100 dilution of stock Mix A or B + 1 mL HNO_3

NOTE: Use Teflon acid dispenser for addition of HNO_3. Prepare all calibration standards in laminar flow hood. The internal standard solution is introduced through manifold: 10:200 dilution of 100 mg/L Rh, 1000 mg/L Pr, and Bi multielement primary stock + 30/200 dilution of Brij 35 stock (stock is 0.25/200 dilution of 30% (w/v) Brij 35). Rh is the internal standard for Li-Cd; Pr is the internal standard for Ba; and Bi is the internal standard for Tl-U. See Appendix 2 for MIX A and MIX B preparation.

Table 7. Linear regression statistics for values versus published values determined by inductively coupled plasma-mass spectrometry

Element	Slope	Intercept	Correlation coefficient
^{27}Al	0.73	11	0.958
^{75}As	0.84	0.1	0.977
^{138}Ba	1.02	-2.1	0.994
^{9}Be	1.4	-0.74	0.961
^{111}Cd	1.2	-0.12	0.993
^{59}Co	1.2	-0.64	0.993
^{52}Cr	1.2	-0.14	0.990
^{65}Cu	0.94	2.4	0.994
^{7}Li	1.3	-1.1	0.972
^{55}Mn	1.1	1.6	0.999
^{95}Mo	1.2	-0.89	0.995
^{60}Ni	1.1	-1.8	0.953
^{208}Pb	0.96	-0.32	0.947
^{88}Sr	0.89	3.4	0.990
^{205}Tl	0.87	0.4	0.867
^{51}V	1.2	-0.65	0.992
^{66}Zn	1.0	0.85	0.969

Table 8. Analytical precision for inductively coupled plasma-mass spectrometric determinations

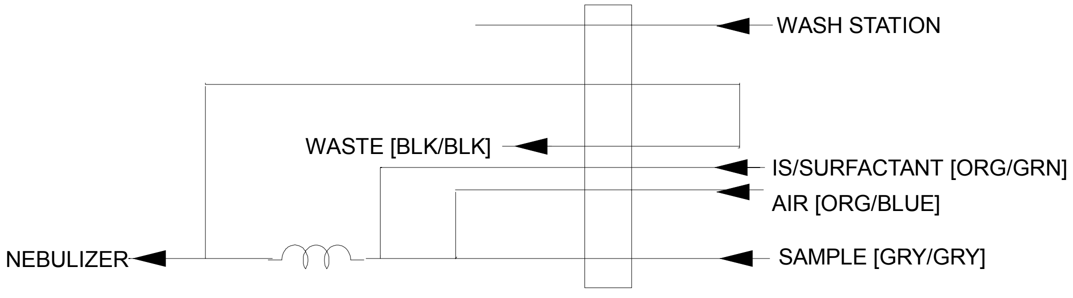
[μg/L, micrograms per liter; %RSD, percent relative standard deviation]

Element	Concentration[1] (μg/L)	Precision[2] %RSD	10 μg/L[3] %RSD	100 μg/L[3] %RSD
^{7}Li	0.08	14	6.8	6.0
^{9}Be	0.10	17	5.7	4.2
^{11}B	2.2	23	6.0	6.8
^{27}Al	1.4	11	7.1	7.2
^{51}V	0.40	10	2.9	1.7
^{52}Cr	1.0	12	4.0	7.2
^{55}Mn	0.30	17	6.2	3.1
^{59}Co	0.05	12	3.8	4.2
^{60}Ni	0.20	17	5.6	4.7
^{63}Cu	0.14	15	7.5	2.4
^{66}Zn	0.36	24	8.3	2.7
^{75}As	3.1	17	7.8	1.2
^{88}Sr	0.06	31	7.2	3.3
^{95}Mo	0.39	13	2.3	1.0
^{111}Cd	0.45	22	4.5	4.6
^{137}Ba	0.53	14	4.9	4.0
^{205}Tl	0.26	12	8.0	8.9
^{208}Pb	0.33	19	6.3	6.0
^{238}U	0.39	14	4.4	1.2

[1] Concentration at about 5 times the detection limit in μg/L.

[2] Percent relative standard deviation at the concentration of 5 times the detection limit.

[3] Percent relative standard deviation at listed concentration.



Pump set at 8.25 units

Pump flow rate 3.0 mL/min

Delivery rate to nebulizer 2.4 mL/min

Sample to waste 0.6 mL/min

MANIFOLD

Alpkem 10-turn mixing coil 303-0310

Alpkem manifold 303-0107-00

Alpkem debubbler 303-0103-00

all 1mm ID

Figure 1. Diagram showing manifold system for internal standards introduction.

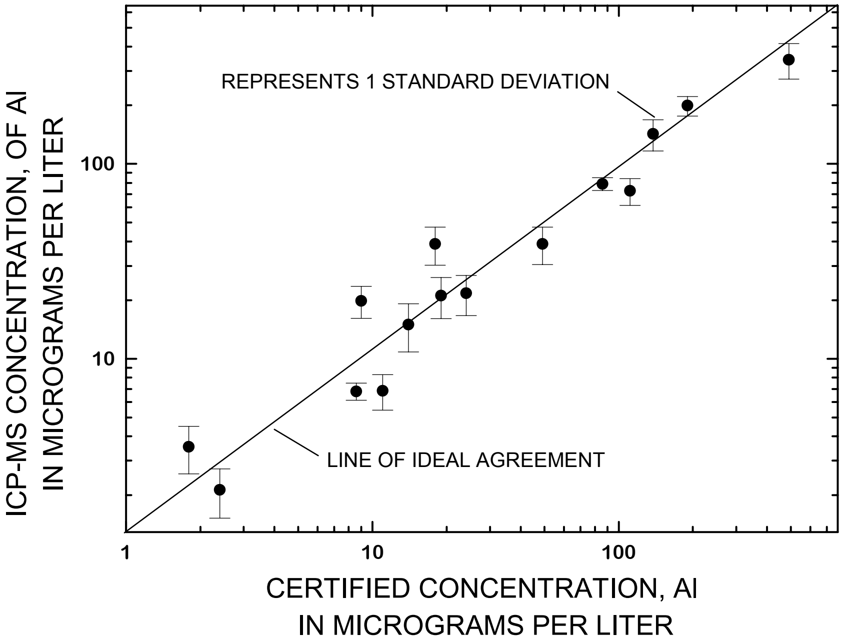


Figure 2. Measured concentrations of aluminum determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

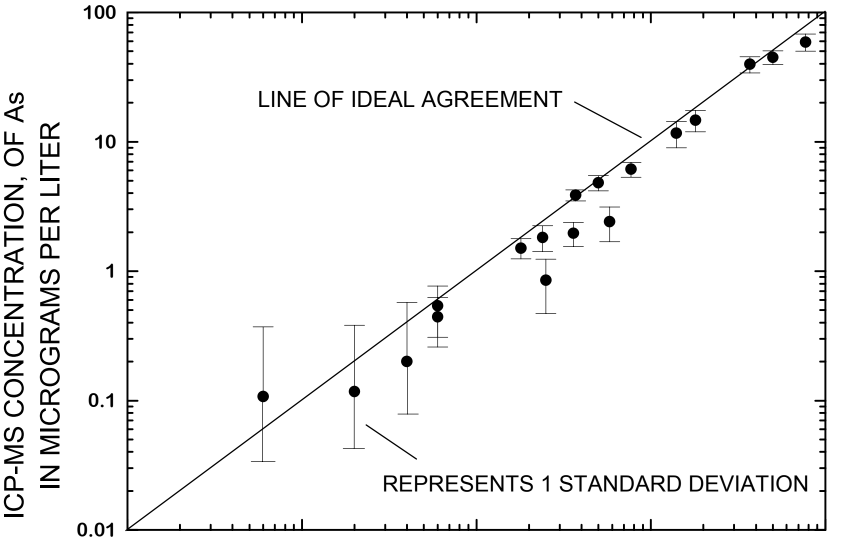


Figure 3. Measured concentrations of arsenic determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

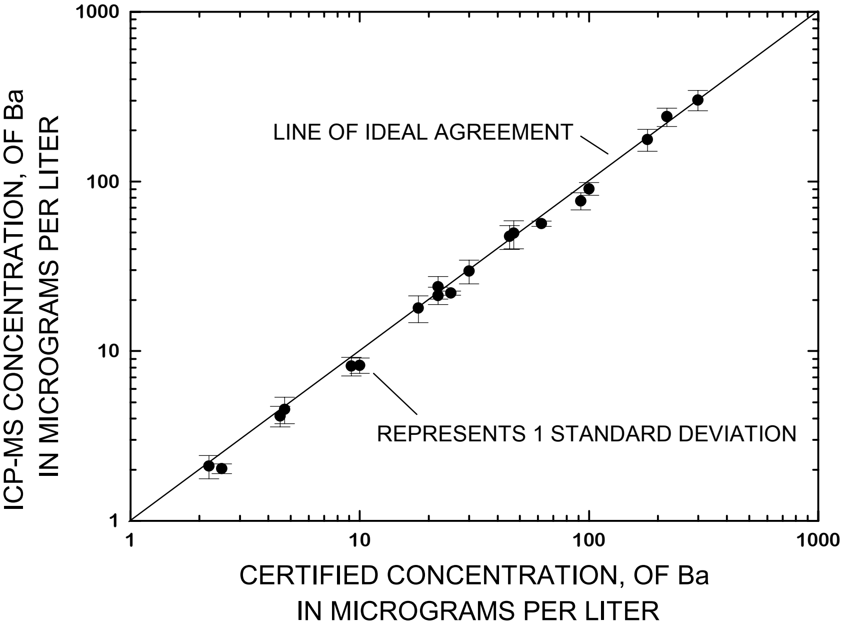


Figure 4. Measured concentrations of barium determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

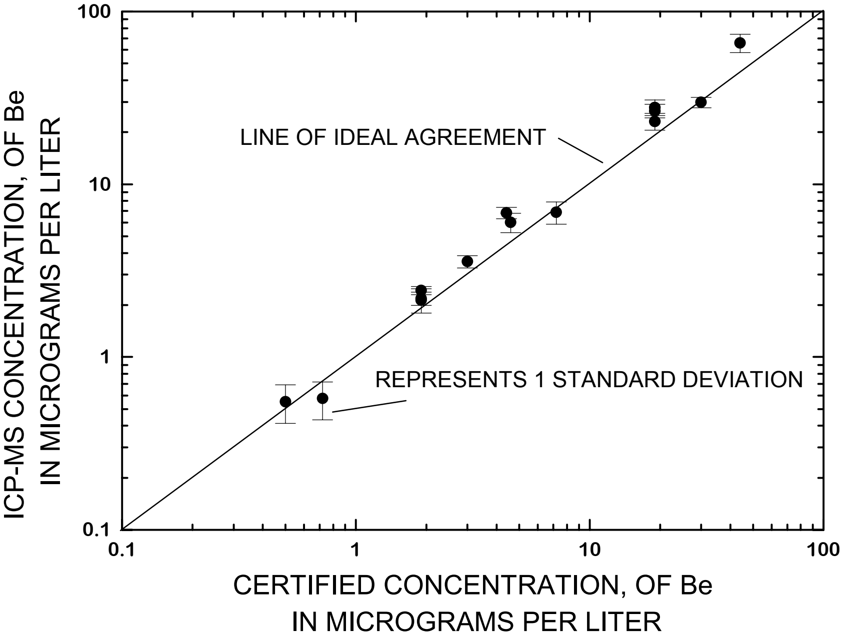


Figure 5. Measured concentrations of determined beryllium by inductively coupled plasma-mass spectrometry for selected reference water standards.

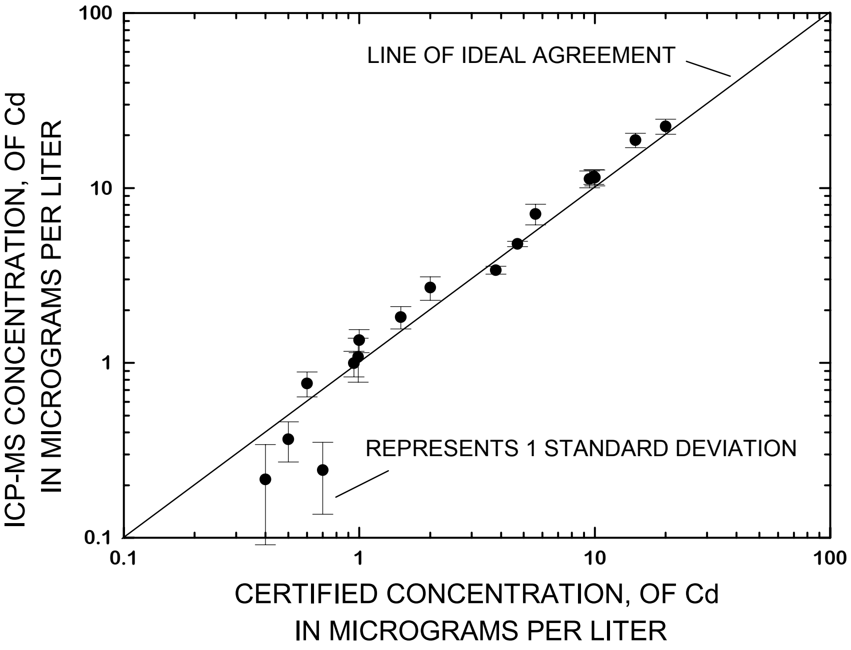


Figure 6. Measured concentrations of cadmium determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

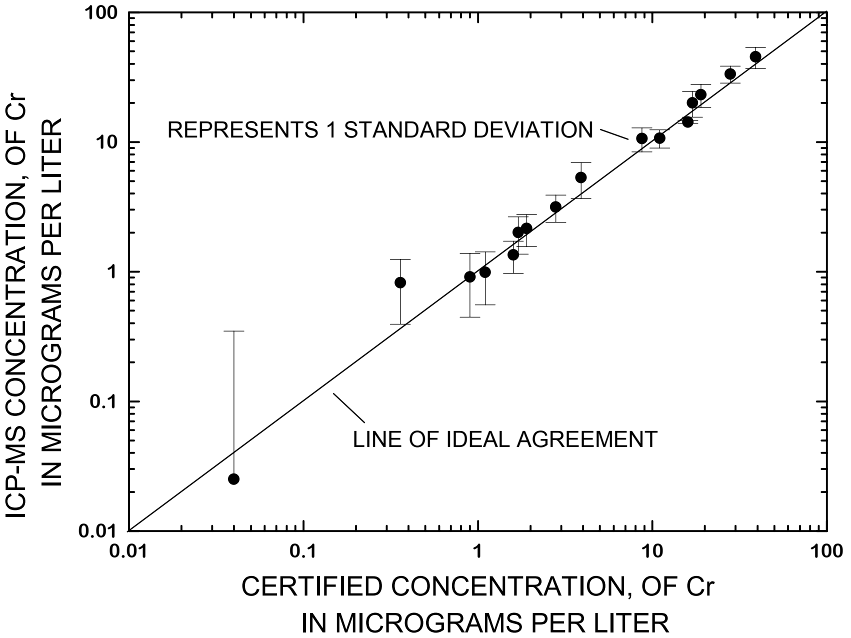


Figure 7. Measured concentrations of chromium determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

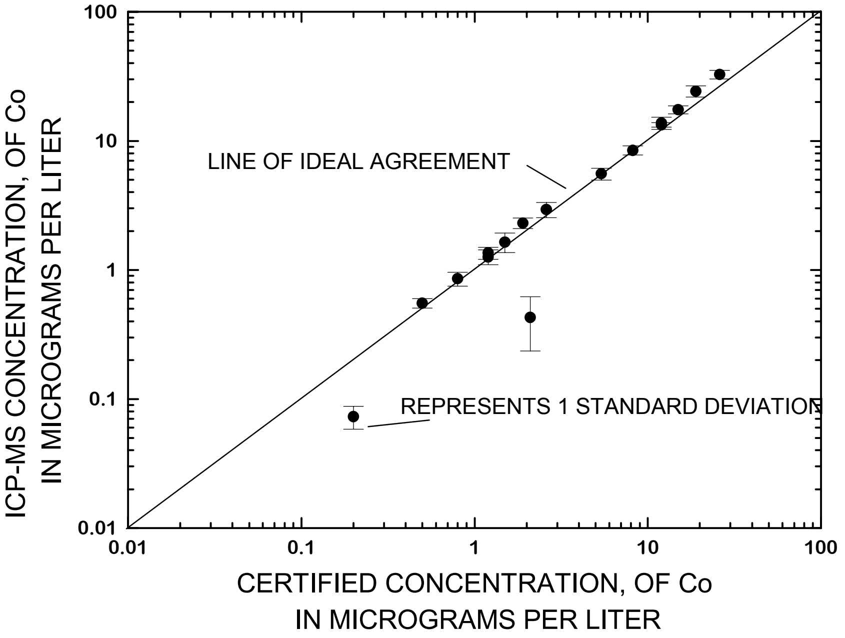


Figure 8. Measured concentrations of cobalt determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

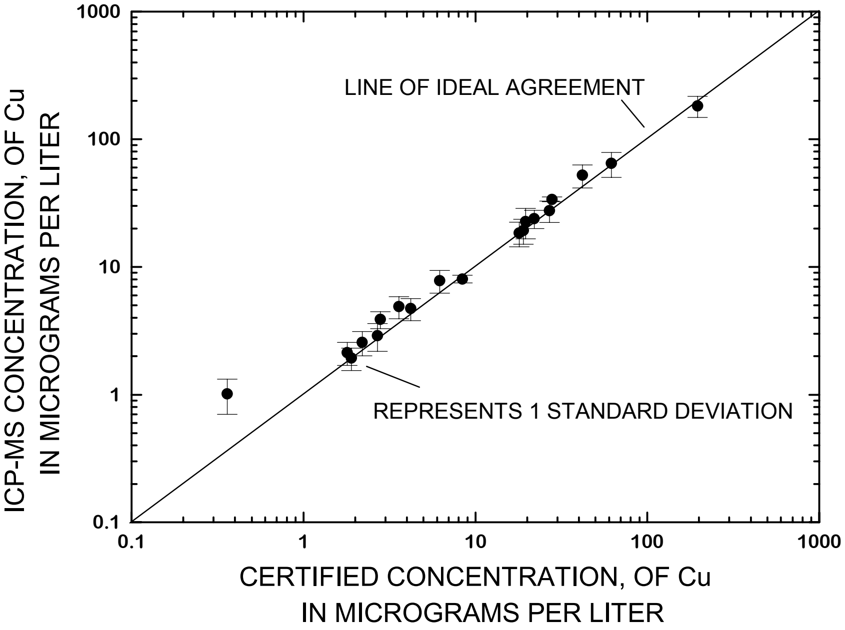


Figure 9. Measured concentrations of copper determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

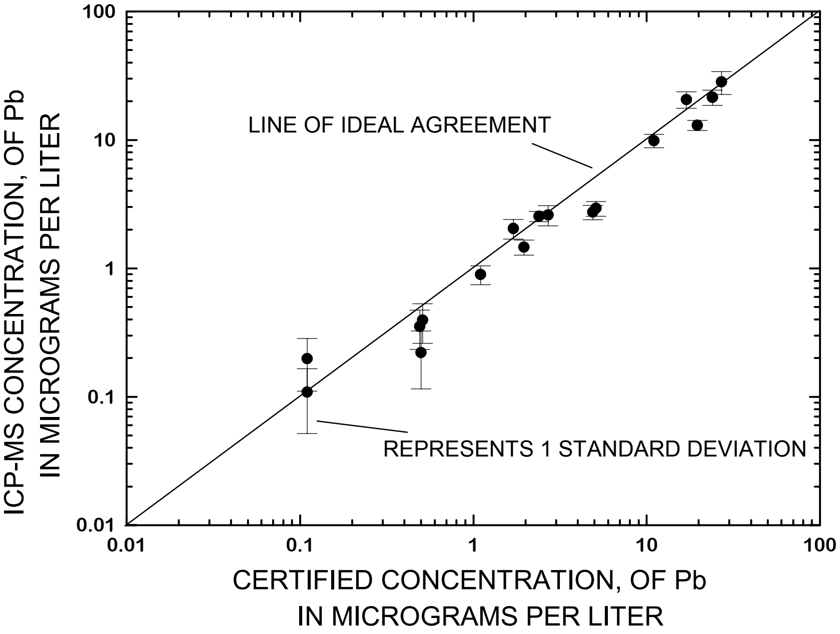


Figure 10. Measured concentrations of lead determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

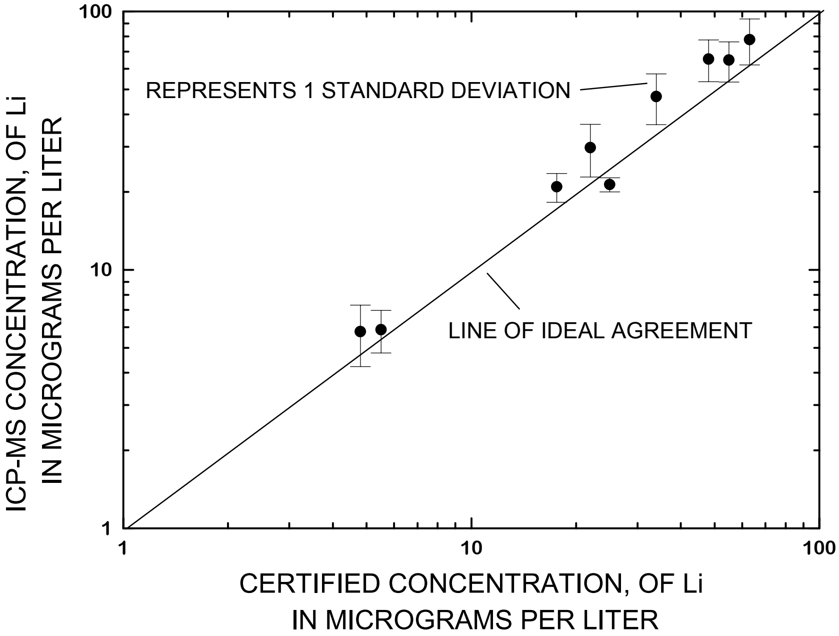


Figure 11. Measured concentrations of lithium determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

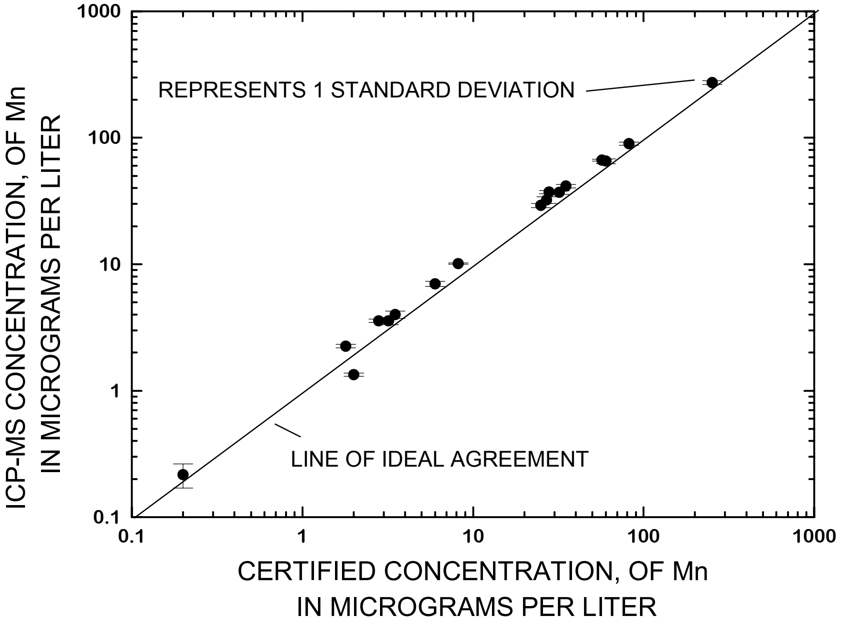


Figure 12. Measured concentrations of manganese determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

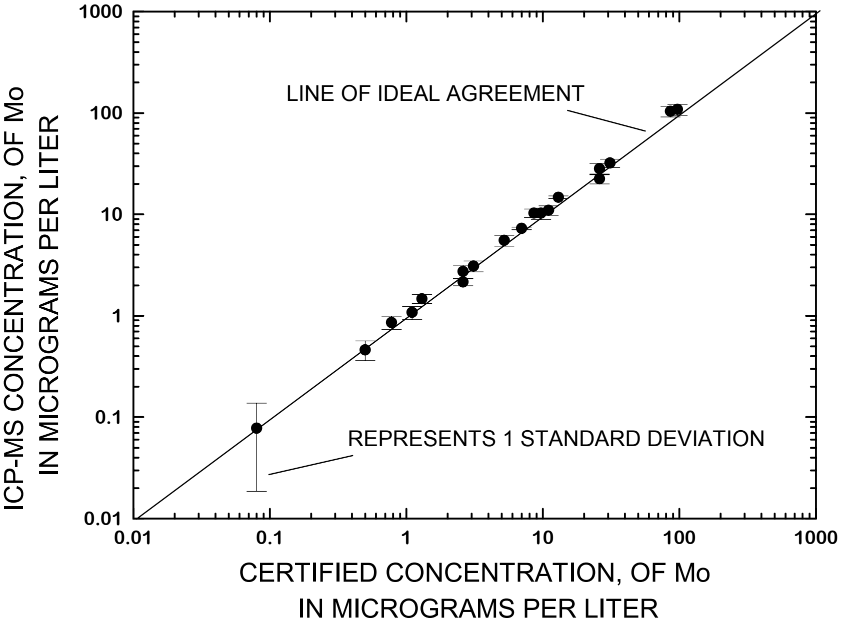


Figure 13. Measured concentrations of molybdenum determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

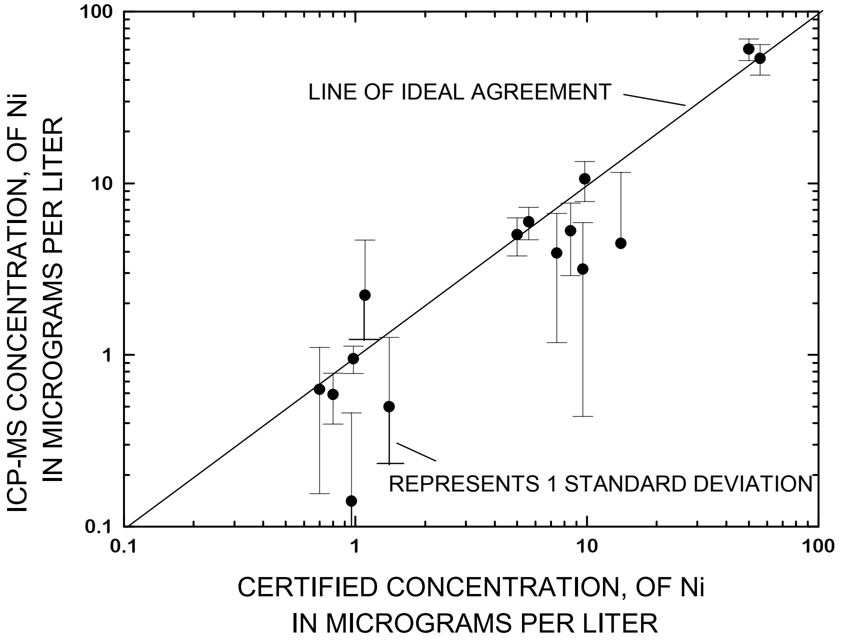


Figure 14. Measured concentrations of nickel by inductively coupled plasma-mass spectrometry for selected reference water standards.

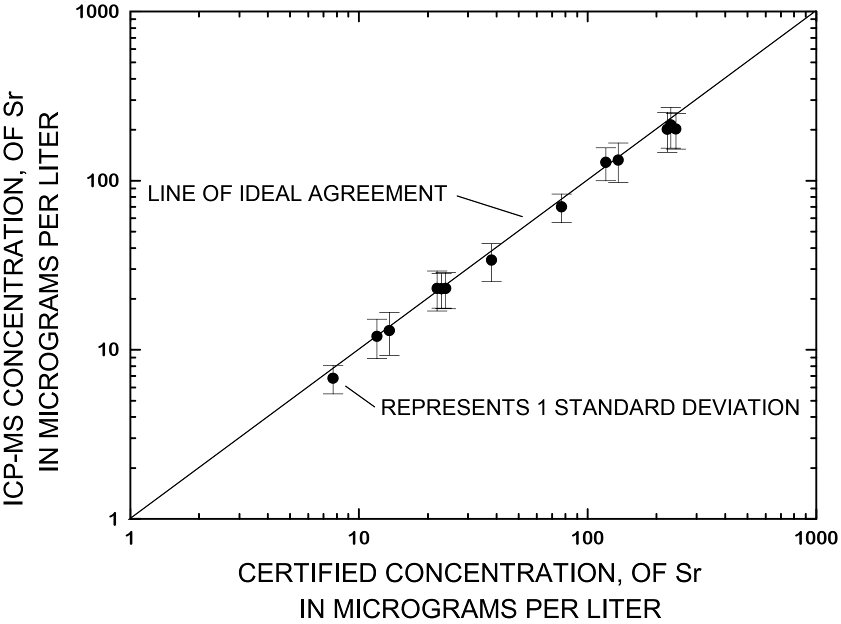


Figure 15. Measured concentrations of strontium determined by determined inductively coupled plasma-mass spectrometry for selected reference water standards.

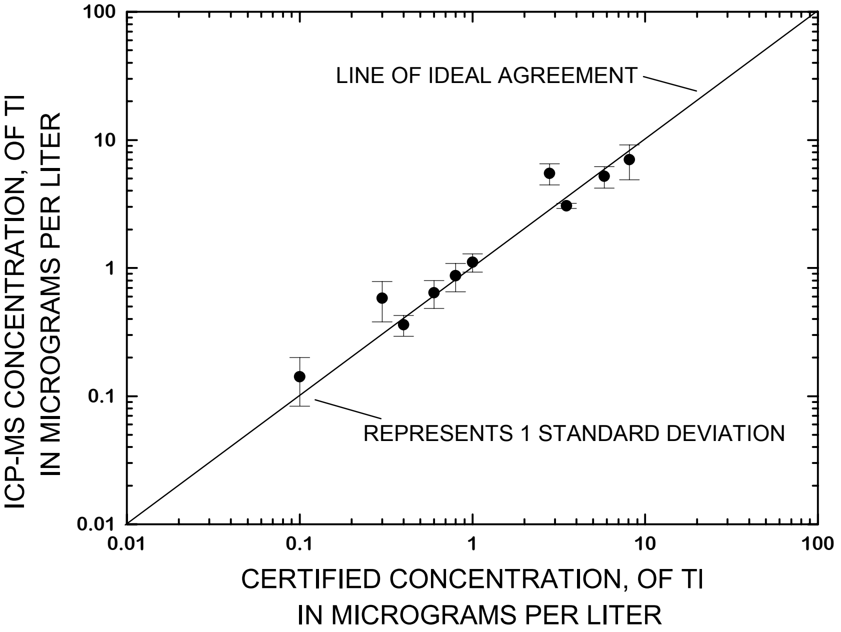


Figure 16. Measured concentrations of thallium determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

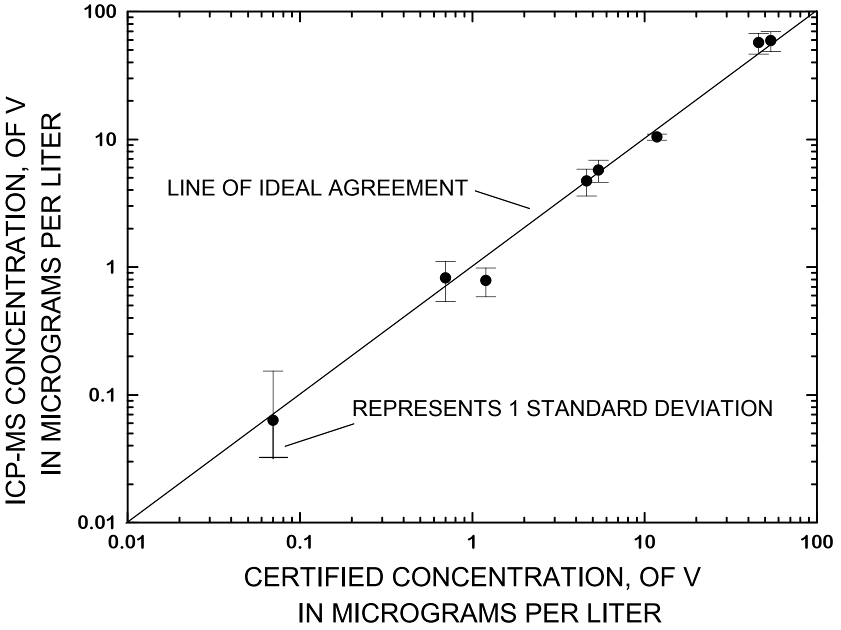


Figure 17. Measured concentrations of vanadium determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

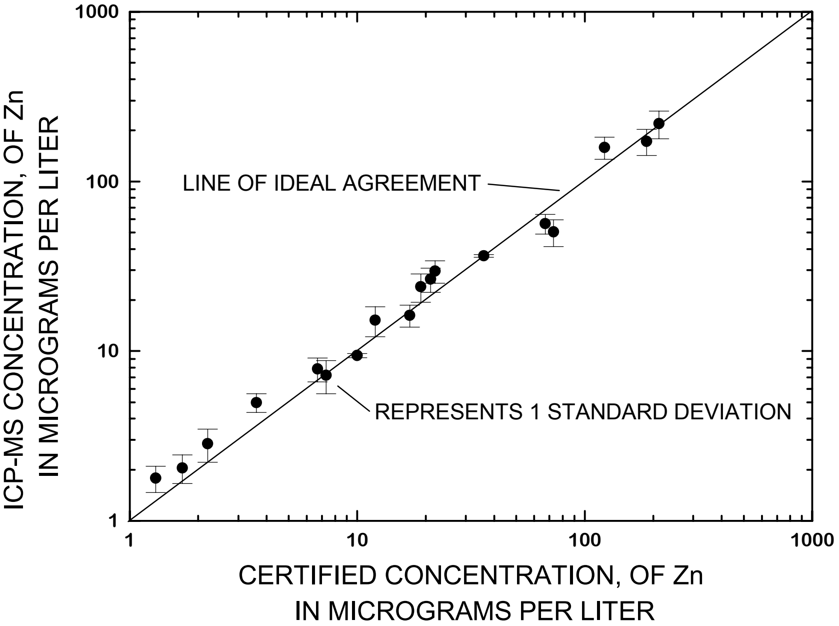


Figure 18. Measured concentrations of zinc determined by inductively coupled plasma-mass spectrometry for selected reference water standards.

APPENDIX 1: Program listing of ICPMS.EXE.

```
      program icpms
c     Revision 1.11
c
c      The purpose of this program is to process analysis
c   results acquired from the ICP-MS as generated through
c   the parameter set 'QA'.  The program requires input
c   files in the 'Summary Report' format.  The sample ID
c   has a 12 alpha-numeric maximum.  All reference standard
c   ID's must begin with *.  In addition, any other sample
c   that should not be included in the sample or QC database
c   should begin with #.  Filenames must follow DOS
c   conventions and be no longer than 8 characters.
c   This program is divided into the following segments:
c        A. Retrieval of 'Summary Report' file
c        B.Processing
c           1.Sorts blank, standard, and sample data from
c             records.
c           2.Calculates linear regression equations for
c             calcium interference on Co and Ni as -
c   Apparent conc (ppb)=Calcium (ppm) X slope + y-intercept
c           3.Corrects for Ca interferences on Ni and Co.
c           4.Checks reference standard results.
c           5.Checks internal standard performance.
c           6.Generates printout of results.
c        C.Generates database records for -
c          1.Samples:  filename.ms
c           a)Substitutes minus detection limits (example
c             -.001) for values that are less than the
c             detection limit.
c           b)Substitutes 999999. for values corresponding
c             to samples that require dilution and rerun.
c          2.QC standards:  filename.qcm
c          3.Saves un-modified mean results:  filename.arc
c        D.Generates text file (filename.txt) for printout
c          via word processor software.
c
c
c   Array variables
c   20=# of analytes.
c   MAXIMUM total number of analyses per run is 50
c        standards(i,20,j) i=1-3 for standards STD1?, STD2?,
c            and STD3? where ? is A and B; j=1 for mean
c            j=2 for standard deviation
c        corr(i,j,k) i=1 for CA50 & i=2 for CA100
c            j=1 for Co & j=2 for Ni; k=1 for mean
```

```
c            k=2 for standard deviation
c        samples(50,20,i) i=1 for mean, i=2 for standard
c             deviation
c        dbase(50,20) database concentrations
c        regs(i,j) i=1 for Co and i=2 for Ni
c             j=1 for y-intercept and j=2 for slope
c        refs(3,20,2) reference standard values; 3=# of std
c             refs; 20=analytes; and 2=mean & stddev
c        sigfact(50,20) sigma values; devs from 1 sigma from
c             the mean value for the reference standard
c             values
c        calcium(50) calcium conc. (ppm) for each sample
c        instd(60,j) internal standard (IS) intensities
c             throughout run; j=1 for Rh, j=2 for Pr, and
c             j=3 for Bi
c        issum(j) sum of all IS intensities; j as above
c        ismean(j) mean of IS intensities; j as above
c        isumsqr(j) sum of the squares of the all the
c             differences between individual IS intensities
c             and the corresponding mean; j as above
c        isdev(j) 1 sigma standard deviations; j as above
c        sigis(50,j) # of sigma deviations from the internal
c             standard mean; j as above
c        comm(50,20) < detection limit string flags
c        comment(50,20) analysis comment, ie 'outside calib'
c        uncorr(50,2) uncorrected Co and Ni concentrations
c        el(20) elemental symbol, string variable
c        dl(20) element detection limit, string variable
c        det(20) element detection limit, numerical
c        sid(50) sample ids, string variable
c   Other variables
c        count counts number of analyses - 1 (for BLANK)
c        nsamp counts number of samples and ref stds
c              analyzed
c        indx  analyte index
c        rindx regression index 1 or 2; Co and Ni
c        con1  low std concentration, 50ppm
c        con2  high std concentration, 100ppm
c        y1    low apparent concentration; Co or Ni
c        y2    high apparent concentration; Co or Ni
c        sigy1 low apparent conc. std dev; Co or Ni
c        sigy2 high apparent conc.std dev; Co or Ni
c        tid   temporary sample id string
c        elem  20 element symbols string
c        limit 20 element detection limit string
c        root  root filename
c   Subroutines
c        stda(indxs,count,standards,instd)
c        stdb(indxs,count,standards,instd)
c        ca(indx,count,corr,instd)
```

```
c        linfit(rindx,con1,con2,y1,sigy1,y2,sigy2,regs)
c   Files
c        msfile:  ICP-MS data file
c        dbfilems.MS: sample results file
c        dbfileqc.QCM: quality control file
c        dbfilearc.ARC: archive file
c        prtfile.TXT: Print file
c   Current reference data for:
c         *SLRS - Canadian standard reference
c         *T103 - SRWS T103
c         *NBS1/10 - 1/10 dilution of NBS1643B
c  --------------------------------------------------------
c
c
      dimension standards(3,20,2),corr(2,2,2)
      dimension samples(50,20,2),regs(2,2)
      dimension calcium(50),uncorr(50,2),det(20)
      dimension sigis(50,3),refs(3,20,2)
      dimension sigfact(50,20),dbase(50,20)
      character*8 root
      character*10 comm(50,20)
      character*12 tid,line*80,answ*1,sid(50)
      character*2 el(20),es,elem*40,limit*80
      character*15 msfile,dbfilems,dbfileqc
      character*15 dbfilearc,comment(50,20),prtfile
      character*4 dl(20),output
      integer rindx,count
      real instd(60,3),issum(3),ismean(3),isumsqr(3),
     +isdev(3)
      elem='LiBeB AlV CrMnCoNiCuZnAsSeSrMoCdBaTlPbU '
      limit='<.03<.02<.4 <.2 <.07<.2 <.06<.01<.03<.02<.08
     +<.6 <3  <.01<.09<.1 <.1 <.05<.06<.06'
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c INITIALIZE COUNTERS                                  c
c LOAD ELEMENTAL SYMBOLS AND DETECTION LIMIT STRINGS  c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      count=0
      nsamp=0
      do 1 i=1,20
      el(i)=elem(i*2-1:i*2)
      dl(i)=limit(i*4-3:i*4)
1     continue
ccccccccccccccccccccccccccccccccccccccccccccccc
c LOAD NUMERICAL ANALYTE DETECTION LIMITS     c
ccccccccccccccccccccccccccccccccccccccccccccccc
      data (det(i),i=1,20)/0.03,0.02,0.4,0.2,0.07,0.2,0.06,
     +0.01,0.03,0.02,0.08,0.6,3.0,0.01,0.09,0.1,0.1,0.05,
     +0.06,0.06/
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c LOAD 1/10 NBS1643b DATA; j=1:MEAN  j=2:STD DEV, N=17    c
```

```
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      data ((refs(1,i,j),j=1,2),i=1,20)/-1.0,-1.0,1.93,
     +0.20,10.1,2.7,-1.0,-1.0,4.68,0.16,1.86,0.15,3.15,0.11,
     +2.82,0.13,5.41,0.30,2.05,0.13,7.18,0.37,-1.0,-1.0,
     +-1.0,-1.0,24.1,0.56,10.2,0.29,2.28,0.10,4.42,0.16,
     +0.76,0.10,2.20,0.32,-1.0,-1.0/
cccccccccccccccccccccccccccccccccccccccccccccccccccc
c LOAD T103 DATA; j=1:MEAN  j=2:STD DEV, N=23      c
cccccccccccccccccccccccccccccccccccccccccccccccccccc
      data ((refs(2,i,j),j=1,2),i=1,20)/30.6,2.6,5.02,0.50,
     +116,14,141,9,42.2,1.8,5.72,0.38,7.86,0.36,4.0,0.14,
     +-1.0,-1.0,79.5,3.6,-1.0,-1.0,3.57,0.78,-1.0,-1.0,
     +-1.0,-1.0,42.0,1.0,2.25,0.16,41.1,0.91,2.74,0.17,
     +9.52,0.62,-1.0,-1.0/
cccccccccccccccccccccccccccccccccccccccccccccccccccc
c LOAD SLRS DATA; j=1:MEAN  j=2:STD DEV, N=18      c
cccccccccccccccccccccccccccccccccccccccccccccccccccc
      data ((refs(3,i,j),j=1,2),i=1,20)/-1.0,-1.0,-1.0,
     +-1.0,-1.0,-1.0,18.4,1.21,0.869,0.24,-1.0,-1.0,
     +1.75,0.08,-1.0,-1.0,-1.0,-1.0,3.65,0.16,1.34,0.20,
     +-1.0,-1.0,-1.0,-1.0,143,4.2,1.18,0.34,-1.0,-1.0,
     +22.4,0.52,-1.0,-1.0,0.209,0.40,0.320,0.06/
ccccccccccccccccccccccccc
c OPEN ICP-MS DATAFILE  c
ccccccccccccccccccccccccc
      print *, 'Enter ICP-MS data file name - '
      read(5,100) msfile
cccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c GET ROOT FOR FILENAME; USED TO NAME DATABASE FILES   c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      k=index(msfile,'.')-1
      root=msfile(1:k)
      open(9,file=msfile)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c START READING RECORDS, KEY ON SAMPLE ID.  STORE      c
c SAMPLE ID IN tid                                     c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccc
10    read(9,105,end=45) line
      if (line(1:10).eq.'Sample ID:') then
        idnl=len(line)-22
        tid=line(23:idnl)
        print *,'....... Processing-',tid
      if (tid.eq.'BLANK'.or.tid.eq.'blank') go to 10
        go to 15
      end if
      go to 10
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c FIND THE START OF CONCENTRATION DATA, LOOK FOR Net Ratio c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
15    read(9,105) line
```

```
      if (line(15:23).ne.'Net Ratio') go to 15
20    read(9,101) es
      if(es.ne.'Li') go to 20
      backspace (unit=9)
ccccccccccccccccccccccccccccccccccccccccccccccccccccc
c POINTER IS AT Li DATA RECORD                      c
c SORT DATA BY SAMPLE ID; STORE IN APPROPRIATE ARRAY  c
ccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccccccccccccccccccccccccccccccccccccc
c DATA CORRESPONDS TO STANDARDS DATA    c
c  STD1A=GROUP A ANALYTES AT 10ppb      c
c  STD2A=GROUP A ANALYTES AT 100ppb     c
c  STD3A=GROUP A ANALYTES AT 500ppb     c
c  SUBSTITUTE B FOR GROUP B ANALYTES    c
ccccccccccccccccccccccccccccccccccccccccc
      if (tid.eq.'STD1A'.or.tid.eq.'std1a') then
        indxs=1
        count=count+1
        call stdsa(indxs,count,standards,instd)
        go to 10
      end if
      if (tid.eq.'STD2A'.or.tid.eq.'std2a') then
        indxs=2
        count=count+1
        call stdsa(indxs,count,standards,instd)
        go to 10
      end if
      if (tid.eq.'STD3A'.or.tid.eq.'std3a') then
        indxs=3
        count=count+1
        call stdsa(indxs,count,standards,instd)
        go to 10
      end if
      if (tid.eq.'STD1B'.or.tid.eq.'std1b') then
        indxs=1
        count=count+1
        call stdsb(indxs,count,standards,instd)
        go to 10
      end if
      if (tid.eq.'STD2B'.or.tid.eq.'std2b') then
        indxs=2
        count=count+1
        call stdsb(indxs,count,standards,instd)
        go to 10
      end if
      if (tid.eq.'STD3B'.or.tid.eq.'std3b') then
        indxs=3
        count=count+1
        call stdsb(indxs,count,standards,instd)
        go to 10
```

```
      end if
ccccccccccccccccccccccccccccccccccccccccccccc
c DATA CORRESPONDS TO CALCIUM STANDARD      c
c   FOR 50ppm Calcium [CA50]                c
c   Cobalt DATA IS corr(1,1,-)              c
c   Nickel DATA IS corr(1,2,-)              c
ccccccccccccccccccccccccccccccccccccccccccccc
      if (tid.eq.'CA50'.or.tid.eq.'ca50') then
        indx=1
        count=count+1
        call ca(indx,count,corr,instd)
        go to 10
      end if
ccccccccccccccccccccccccccccccccccccccccccc
c DATA CORRESPONDS TO CALCIUM STANDARD    c
c   FOR 100ppm Calcium [CA100]            c
c   Cobalt DATA IS corr(2,1,-)            c
c   Nickel DATA IS corr(2,2,-)            c
ccccccccccccccccccccccccccccccccccccccccccc
      if (tid.eq.'CA100'.or.tid.eq.'ca100') then
        indx=2
        count=count+1
        call ca(indx,count,corr,instd)
        go to 10
      end if
ccccccccccccccccccccccccccccccccccccccccccccccccccc
c DATA CORRESPONDS TO SAMPLE, REAGENT BLANK, OR   c
c REFERENCE STANDARDS                             c
c REFERENCE STANDARDS IDENTIFIED BY '*' PREFIX    c
c REAGENT BLANK BY RBLANK                         c
ccccccccccccccccccccccccccccccccccccccccccccccccccc
      count=count+1
      nsamp=nsamp+1
      sid(nsamp)=tid
cccccccccccccccccccccccccc
c GET Li THROUGH Cd DATA c
cccccccccccccccccccccccccc
      do 25 indx=1,16
        read(9,102) samples(nsamp,indx,1),
     +samples(nsamp,indx,2)
25    continue
ccccccccccccccc
c GET Rh DATA c
ccccccccccccccc
      read(9,103) instd(count,1)
ccccccccccccccc
c SKIP A LINE c
ccccccccccccccc
      read(9,105) line
ccccccccccccccc
```

```
c GET Ba DATA c
ccccccccccccccc
      read(9,102) samples(nsamp,17,1),samples(nsamp,17,2)
ccccccccccccccc
c GET Pr DATA c
ccccccccccccccc
      read(9,103) instd(count,2)
ccccccccccccccc
c SKIP A LINE c
ccccccccccccccc
      read(9,105) line
cccccccccccccccccccc
c GET Tl THROUGH U c
cccccccccccccccccccc
      do 35 indx=18,20
         read(9,102) samples(nsamp,indx,1),
     +samples(nsamp,indx,2)
35    continue
ccccccccccccccc
c GET Bi DATA c
ccccccccccccccc
      read(9,103) instd(count,3)
      go to 10
45    close (9)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c CALCULATE CORRECTION REGRESSIONS FOR                    c
c   Apparent Co Conc,ppb vs Calcium Conc,ppm              c
c   rindx=REGRESSION INDEX=1 FOR Cobalt                   c
c   con1=50ppm Ca   y1=AppCo MEAN  sigy1=AppCo STD DEV  c
c   con2=100ppm Ca  y2=AppCo MEAN  sigy2=AppCo STD DEV  c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      rindx=1
      con1=50.0
      con2=100.0
      y1=corr(1,1,1)
      sigy1=corr(1,1,2)
      y2=corr(2,1,1)
      sigy2=corr(2,1,2)
      call linfit(rindx,con1,con2,y1,sigy1,y2,sigy2,regs)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c CALCULATE CORRECTION REGRESSIONS FOR                    c
c   Apparent Ni Conc,ppb vs Calcium Conc,ppm              c
c   rindx=REGRESSION INDEX=2 FOR Nickel                   c
c   con1=50ppm Ca   y1=AppNi MEAN  sigy1=AppNi STD DEV  c
c   con2=100ppm Ca  y2=AppNi MEAN  sigy2=AppNi STD DEV  c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      rindx=2
      con1=50.0
      con2=100.0
      y1=corr(1,2,1)
```

```
      sigy1=corr(1,2,2)
      y2=corr(2,2,1)
      sigy2=corr(2,2,2)
      call linfit(rindx,con1,con2,y1,sigy1,y2,sigy2,regs)
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c ENTER CALCIUM CONCENTRATION VALUES FOR EACH SAMPLE  c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      print *, '---Sample calcium concentraions in PPM---'
      do 50 i=1,nsamp
55    print *, 'Enter Ca conc in ',sid(i),':  '
      read(5,*) calcium(i)
      print *, 'Ca value for ',sid(i),' is ',calcium(i),
     +' value OK ? [N=no]'
      read(5,104) answ
      if (answ.eq.'N'.OR.answ.eq.'n') go to 55
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c CALCULATE CALCIUM CORRECTIONS ON Co (8) AND Ni (9)    c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      if (calcium(i).eq.0) then
        uncorr(i,1)=samples(i,8,1)
        dbase(i,8)=samples(i,8,1)
        uncorr(i,2)=samples(i,9,1)
        dbase(i,9)=samples(i,9,1)
        go to 50
      end if
      uncorr(i,1)=samples(i,8,1)
      samples(i,8,1)=samples(i,8,1)-
     +((regs(1,2)*calcium(i))+regs(1,1))
      if (samples(i,8,1).gt.uncorr(i,1)) then
        samples(i,8,1)=uncorr(i,1)-(regs(1,2)*calcium(i))
      end if
      dbase(i,8)=samples(i,8,1)
      uncorr(i,2)=samples(i,9,1)
      samples(i,9,1)=samples(i,9,1)-
     +((regs(2,2)*calcium(i))+regs(2,1))
      if (samples(i,9,1).gt.uncorr(i,2)) then
        samples(i,9,1)=uncorr(i,2)-(regs(2,2)*calcium(i))
      end if
      dbase(i,9)=samples(i,9,1)
50    continue
ccccccccccccccccccccccccccccccccccccccccccc
c CHECK STANDARD REFERENCE RESULTS        c
c FLAGS RESULTS > 1.5 SIGMA FROM MEAN     c
ccccccccccccccccccccccccccccccccccccccccccc
      do 60 i=1,nsamp
      if (sid(i).eq.'*NBS1/10') then
        nref=1
        go to 65
      end if
      if (sid(i).eq.'*T103') then
```

```
          nref=2
          go to 65
        end if
        if (sid(i).eq.'*SLRS') then
          nref=3
          go to 65
        end if
        go to 60
65      do 70 j=1,20
        if (refs(nref,j,1).eq.-1.0) then
          sigfact(i,j)=-1.0
          comm(i,j)='N/A'
          comment(i,j)=''
          go to 70
        end if
        sigfact(i,j)=abs(samples(i,j,1)-refs(nref,j,1))/
       +refs(nref,j,2)
        if (sigfact(i,j).gt.1.5) then
          comm(i,j)='>1.5sigma'
          comment(i,j)=''
          go to 70
        end if
        comm(i,j)=''
        comment(i,j)=''
70      continue
60      continue
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c INSERT MINUS DETECTION LIMIT VALUES FOR CONCENTRATIONS  c
c LESS THAN OR EQUAL TO THE DETECTION LIMIT AND CHECK FOR c
c VALUES OUTSIDE THE CALIBRATION RANGE                     c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
        do 225 i=1,nsamp
        m=index(sid(i),'*')
        if (m.ne.0) go to 225
        do 230 j=1,20
        if (samples(i,j,1).le.det(j)) then
          dbase(i,j)=det(j)*(-1.)
          comm(i,j)=dl(j) // 'ppb'
          go to 230
        end if
        if (samples(i,j,1).gt.500.) then
          dbase(i,j)=999999.
          comment(i,j)='outside range'
          go to 230
        end if
        dbase(i,j)=samples(i,j,1)
        comm(i,j)=''
        comment(i,j)=''
230     continue
225     continue
```

```
cccccccccccccccccccccccccccccccccccccc
c   ******** OUTPUT AREA ********    c
cccccccccccccccccccccccccccccccccccccc
c
cccccccccccccccccccccccccccccccccccccc
c   PRINTER OUTPUT                   c
cccccccccccccccccccccccccccccccccccccc
      k=index(root,' ')-1
      prtfile=root(1:k)//'.txt'
      print *, '....... Making print file ',prtfile
      open(9,file=prtfile)
      write(9,891) msfile
891   format('ICP-MS RESULTS FOR FILE ',a15)
      write(9,812)
      write(9,900)
900   format('---- Calibration Data ----')
      write(9,905)
905   format('Standard',1x,'Analyte',1x,'Conc.,ppb',2x,
     +'Inten. Ratio')
      write(9,811)
      do 910 i=1,3
      do 915 j=1,20
      write(9,920) i,el(j),standards(i,j,1),standards(i,j,2)
920   format('STD',i1,'A/B',5x,a2,3x,e10.4,1x,e10.4)
915   continue
      write(9,812)
910   continue
      write(9,812)
      write(9,875)
875   format('---- Calcium Interfence Equations ----')
      write(9,880) regs(1,2),regs(1,1)
880   format('AppCo(ppb)=',e10.4,' X Ca(ppm) + ',e10.4)
      write(9,885) regs(2,2),regs(2,1)
885   format('AppNi(ppb)=',e10.4,' X Ca(ppm) + ',e10.4)
      write(9,812)
      write(9,811)
      do 80 i=1,nsamp
      write(9,805) sid(i)
805   format('Sample:  ',a12)
      write(9,830) calcium(i)
830   format('Calcium concentration = ',f8.4,' ppm')
      write(9,835) uncorr(i,1)
      write(9,840) uncorr(i,2)
835   format('UnCorrected Co = ',e10.4,' ppb')
840   format('UnCorrected Ni = ',e10.4,' ppb')
ccccccccccccccccccccccccccccccccccccccccccccc
c   CHECK IF SAMPLE IS REFERENCE MATERIAL   c
ccccccccccccccccccccccccccccccccccccccccccccc
      m=index(sid(i),'*')
      if (m.eq.0) go to 87
```

```
      write(9,841)
841   format(6x,'Conc,ppb',3x,'SD,ppb',
     +5x,'SIGMA')
      write(9,811)
      do 85 j=1,20
      if (sigfact(i,j).eq.-1.0) then
        write(9,844) el(j),samples(i,j,1),samples(i,j,2),
     +comm(i,j),comment(i,j)
844     format(a2,3x,1pe10.3,1x,e10.3,2x,a10,1x,a15)
        go to 85
      end if
      write(9,843) el(j),samples(i,j,1),samples(i,j,2),
     +sigfact(i,j),comm(i,j)
843   format(a2,3x,1pe10.3,1x,e10.3,1x,e8.2,1x,a10)
85    continue
      write(9,812)
      go to 80
87    write(9,810)
810   format(6x,'Conc,ppb',3x,'SD,ppb',5x,'Comments')
      write(9,811)
811   format(60('-'))
      do 90 j=1,20
       write(9,815) el(j),samples(i,j,1),samples(i,j,2),
     +comm(i,j),comment(i,j)
815   format(a2,3x,1pe10.3,1x,e10.3,1x,a10,1x,a15)
90    continue
      write(9,812)
812   format(1x)
80    continue
cccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c   LIST ANALYSIS INTERNAL STANDARD VALUES AND EACH    c
c   CORRESPONDING DEVIATION FROM MEAN                  c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c
ccccccccccccccccccc
c CALCULATE SUMS  c
ccccccccccccccccccc
      do 150 j=1,3
      do 155 i=1,count
      issum(j)=issum(j)+instd(i,j)
155   continue
150   continue
      do 160 j=1,3
      ismean(j)=issum(j)/count
160   continue
cccccccccccccccccccccccccccccccccccc
c  CALCULATE STANDARD DEVIATIONS  c
cccccccccccccccccccccccccccccccccccc
      do 165 j=1,3
      do 170 i=1,count
```

```
      isumsqr(j)=isumsqr(j)+(instd(i,j)-ismean(j))**2
170   continue
165   continue
      do 175 j=1,3
      isdev(j)=sqrt(isumsqr(j)/(count-1))
175   continue
cccccccccccccccccccccccccccccccccccccccc
c CALCULATE # OF SIGMAS FROM THE MEAN  c
cccccccccccccccccccccccccccccccccccccccc
      do 180 j=1,3
      do 185 i=1,nsamp
      sigis(i,j)=abs(instd(i+(count-nsamp-1),j)-
     +ismean(j))/isdev(j)
185   continue
180   continue
      write(9,812)
      write(9,811)
      write(9,190)
190   format('+++ INTERNAL STANDARDS REPORT +++')
      write(9,191)
191   format('Sample ID',4x,'Rh',7x,'Pr',7x,'Bi')
      write(9,811)
      write(9,194) (ismean(j),j=1,3)
194   format('Mean',9x,1pe8.2,1x,e8.2,1x,e8.2)
      write(9,195) (isdev(j),j=1,3)
195   format('1 Sigma',6x,1pe8.2,1x,e8.2,1x,e8.2)
      write(9,196)
196   format('Fraction of 1 sigma values')
      do 192 i=1,nsamp
      write(9,193) sid(i),sigis(i,1),sigis(i,2),
     +sigis(i,3)
193     format(a12,1x,1pe8.2,1x,e8.2,1x,e8.2)
        go to 192
192   continue
      close (9)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c DATABASE OUTPUT - SAMPLES (device 9) AND QC (device 10)c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      k=index(root,' ')-1
      dbfilems=root(1:k)//'.ms'
      dbfileqc=root(1:k)//'.qcm'
      print *, '....... Making ms file=',dbfilems
      print *, '....... Making qc file=',dbfileqc
      open(9,file=dbfilems)
      open(10,file=dbfileqc)
      write(9,821) root
      write(10,821) root
821   format(a8)
      write(9,820) (el(i),i=1,20)
      write(10,820) (el(i),i=1,20)
```

```
820   format('ID',20(1x,a2))
      do 200 i=1,nsamp
cccccccccccccccccccccccccccccccccccccccccccccccccccccc
c IF # IS FOUND IN THE ID DON'T SAVE RESULTS TO DATABASE c
c IF * IS FOUND IN THE ID SAVE IT TO THE QC DATABASE     c
c IF NIETHER IS FOUND SAVE IT TO THE SAMPLE DATABASE     c
cccccccccccccccccccccccccccccccccccccccccccccccccccccc
      n=index(sid(i),'#')
      if (n.ne.0) go to 200
      m=index(sid(i),'*')
      if (m.ne.0) then
        write(10,825) sid(i),(samples(i,j,1),j=1,20)
        go to 200
      end if
      write(9,825) sid(i),(dbase(i,j),j=1,20)
825   format(a12,1x,20(1pe10.3,1x))
200   continue
      endfile (9)
      close (9)
      endfile (10)
      close (10)
cccccccccccccccccccc
c   ARCHIVE OUTPUT c
cccccccccccccccccccc
      dbfilearc=root(1:k)//'.arc'
      open(9,file=dbfilearc)
      do 205 i=1,20
      do 210 j=1,3
      write(9,106) standards(j,i,1),standards(j,i,2)
210   continue
      write(9,115)
      do 215 m=1,nsamp
      write(9,108) sid(m),samples(m,i,1),samples(m,i,2)
215   continue
205   continue
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c   WRITE CORRECTION DATA I=1 FOR CA50 AND I=2 FOR CA100; c
c   corr(i,1,x)=Co AND corr(i,2,x)=Ni                     c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      write(9,111)
      do 220 i=1,2
      write(9,106) corr(i,1,1),corr(i,1,2)
      write(9,106) corr(i,2,1),corr(i,2,2)
220   continue
      write(9,112)
      write(9,110) regs(1,1),regs(1,2)
      write(9,113)
      write(9,110) regs(2,1),regs(2,2)
      endfile (9)
      close (9)
```

```
100   format(a15)
101   format(a2)
102   format(36x,f11.3,1x,f11.3)
103   format(18x,f6.0)
104   format(a1)
105   format(a80)
106   format(e10.4,1x,e10.4,1x,e10.4)
107   format(i4)
108   format(a12,1x,e10.4,1x,e10.4,1x,e10.4)
109   format(e10.4,1x,e10.4,1x,e10.4,1x,e10.4)
110   format('Yinter= ',e10.4,3x,'slope= ',e10.4)
111   format('--- Co & Ni Correction Equations ---')
112   format('Equations for Co correction')
113   format('Equations for Ni correction')
115   format('Status,IR,and SD data for samples')
      stop
      end
c-----------------------------------------------------------
c***********************************************************
c    *** SUBROUTINE STDSA ***                              *
c    PUTS DATA FOR GROUP A ANALYTES INTO ARRAY             *
c    standards(indxs,indx,m)                               *
c    WHERE indxs IS THE STANDARD INDEX #, indx IS          *
c    THE ANALYTE INDEX NUMBER, AND m=1 FOR mean, 2 FOR     *
c    std dev                                               *
c***********************************************************
      subroutine stdsa(indxs,count,standards,instd)
      dimension standards(3,20,2)
      character line*80
      integer count
      real instd(60,3)
c
c GET Li THROUGH Al DATA
c
      do 300 indx=1,4
        read(9,305) standards(indxs,indx,1),
     +standards(indxs,indx,2)
305     format(36X,F11.3,1X,f11.3)
300   continue
c
c SKIP V DATA
c
      read(9,310) line
310   format(a80)
c
c GET Cr THROUGH Zn DATA
c
      do 315 indx=6,11
        read(9,305) standards(indxs,indx,1),
     +standards(indxs,indx,2)
```

```
315   continue
c
c SKIP As AND Se DATA
c
      read(9,310) line
      read(9,310) line
c
c GET Sr DATA
c
      read(9,305) standards(indxs,14,1),
     +standards(indxs,14,2)
c
c GET Mo DATA
c
      read(9,305) standards(indxs,15,1),
     +standards(indxs,15,2)
c
c GET Cd DATA
c
      read(9,305) standards(indxs,16,1),
     +standards(indxs,16,2)
c
c GET Rh DATA
c
      read(9,320) instd(count,1)
320   format(18x,f6.0)
c
c SKIP A LINE
c
      read(9,310) line
c
c GET Ba DATA
c
      read(9,305) standards(indxs,17,1),
     +standards(indxs,17,2)
c
c GET Pr DATA
c
      read(9,320) instd(count,2)
c
c SKIP A LINE
c
      read(9,310) line
c
c GET Tl THROUGH U
c
      do 325 indx=18,20
        read(9,305) standards(indxs,indx,1),
     +standards(indxs,indx,2)
325   continue
```

```
c
c GET Bi DATA
c
      read(9,320) instd(count,3)
      return
      end
c----------------------------------------------------------
c----------------------------------------------------------
c**********************************************************
c   *** SUBROUTINE STDSB ***                              *
c   PUTS DATA FOR B GROUP ANALYTES INTO ARRAY             *
c   standards(indxs,indx,m)                               *
c   WHERE indxs IS THE STANDARD INDEX #, indx IS          *
c   THE ANALYTE INDEX NUMBER, AND m=1 FOR mean, 2 FOR     *
c   std dev                                               *
c**********************************************************
      subroutine stdsb(indxs,count,standards,instd)
      dimension standards(3,20,2)
      character line*80
      integer count
      real instd(60,3)
c
c SKIP TO V DATA
c
      do 415 i=1,4
        read(9,400) line
400     format(a80)
415   continue
c
c GET V DATA
c
      read(9,405) standards(indxs,5,1),
     +standards(indxs,5,2)
405   format(36x,f11.3,1x,f11.3)
c
c SKIP TO As and Se DATA
c
      do 420 i=1,6
        read(9,400) line
420   continue
c
c GET As AND Se DATA
c
      read(9,405) standards(indxs,12,1),
     +standards(indxs,12,2)
      read(9,405) standards(indxs,13,1),
     +standards(indxs,13,2)
c
c SKIP TO Mo DATA
c
```

```
      read(9,400) line
c
c SKIP Mo DATA
c
      read(9,400) line
c
c SKIP TO Rh DATA
c
      read(9,400) line
c
c GET Rh DATA
c
      read(9,410) instd(count,1)
410   format(18x,f6.0)
c
c SKIP TO Pr DATA
c
      read(9,400) line
      read(9,400) line
c
c GET Pr DATA
c
      read(9,410) instd(count,2)
c
c SKIP TO Bi DATA
c
      do 425 i=1,4
        read(9,400) line
425   continue
c
c GET Bi DATA
c
      read(9,410) instd(count,3)
      return
      end
c----------------------------------------------------------
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c   *** SUBROUTINE LINFIT ***                            c
c   SUBROUTINE CALCULATES LINEAR REGRESSION EQUATIONS     c
c   FOR THE CALIBRATION CURVES.                          c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine linfit(rindx,con1,con2,y1,
     +sigy1,y2,sigy2,regs)
      double precision sum,sumx,sumy,sumx2,sumxy,sumy2
      double precision xx,yy,weight,delta
      dimension regs(2,2),x(2),y(2),sigmay(2)
      integer rindx
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c   ACCUMULATE WEIGHTED SUMS BASED ON INSTRU VARIANCE      c
c   x(1)=LOW CONC y(1)=LOW INTENSITY RATIO = regs(-,-,3)   c
```

```
c   x(2)=HIGH CONC y(2)=HIGH INTENSITY RATIO = regs(-,-,4) c
c   sigmay(1)=STD DEV OF y(1) & sigmay(2)=STD DEV OF y(2)  c
c   Y-INTERCEPT = regs(-,-,1)                              c
c   SLOPE = regs(-,-,2)                                    c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      x(1)=con1
      x(2)=con2
      y(1)=y1
      y(2)=y2
      sigmay(1)=sigy1
      sigmay(2)=sigy2
      sum=0
      sumx=0
      sumy=0
      sumx2=0
      sumxy=0
      sumy2=0
      do 500 i=1,2
      xx=x(i)
      yy=y(i)
      weight=1.0/sigmay(i)**2
      sum=sum+weight
      sumx=sumx+weight*xx
      sumy=sumy+weight*yy
      sumx2=sumx2+weight*xx*xx
      sumxy=sumxy+weight*xx*yy
      sumy2=sumy2+weight*yy*yy
500   continue
c
c CALCULATE REGRESSION COEFFICIENTS AND STD. DEVS
c   regs(-,1) = Y-INTERCEPT
c   regs(-,2) = SLOPE
c
      delta=sum*sumx2-sumx*sumx
      regs(rindx,1)=(sumx2*sumy-sumx*sumxy)/delta
      regs(rindx,2)=(sumxy*sum-sumx*sumy)/delta
      return
      end
c-----------------------------------------------------------
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c   *** SUBROUTINE CA ***                                  c
c RETRIEVES APPARENT CONCENTRATION VALUES FOR Co AND Ni    c
c DUE TO Ca AT CONCENTRATIONS OF 50 AND 100 PPM            c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c
      subroutine ca(indx,count,corr,instd)
      dimension corr(2,2,2)
      integer count
      real instd(60,3)
      character line*80
```

```
c
c SKIP TO Co DATA
c
      do 600 i=1,7
        read(9,605) line
605     format(a80)
600   continue
c
c GET Co AND Ni DATA
c
      read(9,610) corr(indx,1,1),corr(indx,1,2)
610   format(36x,f11.3,1x,f11.3)
      read(9,610) corr(indx,2,1),corr(indx,2,2)
c
c SKIP TO Rh DATA
c
      do 620 i=1,7
        read(9,605) line
620   continue

c
c GET Rh DATA
c
      read(9,615) instd(count,1)
615   format(18x,f6.0)
c
c SKIP TO Pr DATA
c
      read(9,605) line
      read(9,605) line
c
c GET Pr DATA
c
      read(9,615) instd(count,2)
c
c SKIP TO Bi DATA
c
      do 625 i=1,4
        read(9,605) line
625   continue
c
c GET Bi DATA
c
      read(9,615) instd(count,3)
      return
      end
```

APPENDIX 2: Preparation of primary multielement stock solutions.

All single element stock solutions are NBS Standard Solutions except Sr, As, and Mo either because of the lack of a standard or because of the presence of chloride.

REAGENT BLANK

10 percent HNO_3 (V/V) in deionized water.

Mixed element calibration standard A

10,000 mg/L single element NBS stock (1/1000)=10 mg/L for Li, Be, Al, Cr, Mn, Co, Ni, Cu, Zn, Cd, Ba, Tl, Pb, and U.

1,000 mg/L Sr lab stock (10/1000)=10 mg/L

5,000 mg/L B NBS stock (2/1000)=10 mg/L

Brought to volume and acidified with 100 mL HNO_3 (10%)

Mixed element calibration standard B

5,000 mg/L V NBS stock (2/1000)=10 mg/L

1,000 mg/L As lab stock (10/1000)=10 mg/L

10,000 mg/L Mo lab stock (1/1000)=10 mg/L

Brought to volume and acidified with 100 mL HNO_3 (10%)

Interference correction standard CA50

1000 mg/L Ca stock (5/100)=50 mg/L Ca

Brought to volume with 10 % (V/V) HNO_3

Interference correction standard CA100

1000 mg/L Ca stock (10/100)=100 mg/L Ca

Brought to volume with 10 % (V/V) HNO_3

APPENDIX 3: User instructions for inductively coupled plasma-mass spectrometry instrument operation.

Replace peristaltic pump tubing if needed (every other day).

Clean peristaltic pump rollers with silicon (daily).

Start peristaltic pump and adjust pressure if bubble period is not uniform.

Pump surfactant to nebulizer and insure that massflow controller reads 59-59.3. If it doesn't, use syringe to clean nebulizer.

Ignite plasma. Set alarm level to about 8. Switch reflected on.

Allow instrument to equilibrate for at least 1 hour.

Prepare the following solutions

(Those with asterisk * - prepare every other day)

*Calibration standards (see APPENDIX 2)

Dose each with 2 X 0.5 mL nitric acid from dosing dispenser

BLANK	Reagent blank, nitric acid in deionized water
STD1A and STD1B	STD2A or STD2B X (10/100)= 0.01 mg/L or 10 µg/L
STD2A and STD2B	10 mg/L stock A or B X (1/100)=0.1 mg/L or 100 µg/L
STD3A and STD3B	10 mg/L stock A or B X (5/100)=0.5 mg/L or 500 µg/L

Internal standard (IS) stock solution

Dose each with 2 X 0.5 mL nitric acid from dosing dispenser

Rh 100 mg/L stock X (0.1/100) = 0.10 mg/L

Pr 100 mg/L stock X (1/100) = 1.0 mg/L

Bi 1000 mg/L stock X (0.1/100) = 1.0 mg/L

* Internal standard working solution

Dose with 4 X 0.5 mL nitric acid from dosing dispenser

Dilute IS stock solution 10/200 + 30 mL surfactant solution

* Working surfactant solution (surfactant only)

Dose each with 4 X 0.5mL nitric acid from dosing dispenser

Dilute surfactant solution 30/200 in deionized water

Surfactant solution

Dilute 30% Brij 35 250 mL/200 mL in deionized water

Calcium solutions

Dose each with 2 X 0.5 mL nitric acid from dosing dispenser

CA50 1000 mg/L Ca stock X (5/100)=50 mg/L Ca

CA100 1000 mg/L Ca stock X (10/100)=100 mg/L Ca

* 1/10 dilution of NBS1643b

(dosing not needed)

Rinse solution

About 1% (volume) nitric acid.

Tuning solution

Dilute 1000 mg/L Li,Rh, and Pb stock 10/100

Tune ion optics:

Execute the following ICPMS program commands

- <UTILITIES>
  - <CONFIGURATION>
    - <F6> next window
    - Answer No to autosampler
    - <F3> close application
- <APPLICATIONS>
  - <GRAPHICS>
    - Parameter set 'setup' should be loaded (if not, load it by entering File/Open data set 'setup')
    - Enter date for sample ID and enter 'sample' as type; for example, 12Nov91.
    - Place sipper in tuning solution.
    - Enter <F12> to begin analysis, display of signal intensity versus time will be plotted in realtime.
    - Equalize signal from Pb and Li, maximize signal from Rh by adjusting the P and S2 lens digipots a few unit up or down. From day to day the magnitude of the signals will degrade somewhat. Cryoclean should be scheduled once a week to restore signals.
    - When finished tuning, stop analysis using shift<F11>
    - Use <F3> to close application.

<UTILITIES>

<CONFIGURATION>

<F6> next window

Yes to autosampler; autosampler control code will be downloaded to the autosampler.

<F3> close application.

Sample analysis:

<APPLICATIONS>

<QUANT ANALYSIS>

Parameter set 'qa' should be loaded.

Open new datafile:

[File]-open new data set

Filename: choose filename, enter data description if desired, For example 'MYDATA'

[File] [Copy sample Information]. Select 'template'.

Enter analysis sequence for unknowns as follows:

Sample ID	TYPE	Seq.#	AS Pos.
BLANK	blank	1	49
STD1A	standard	1	50
STD2A	standard	1	51
STD3A	standard	1	52
STD1B	standard	1	53
STD2B	standard	1	54
STD3B	standard	1	55
*NBS1/10	sample	1	1
*SLRS	sample	1	2
*T103	sample	1	3
3345	sample	1	4
.	.	.	.
.	.	.	.
.	.	.	.
CA50	sample	1	56
CA100	sample	1	57

Use NBS1643b, T103, or SLRS for reference standards. These must have identifications as '*NBS1/10', '*T103', and '*SLRS' so that they are sorted into the QC database. Unknown samples will be placed into the Sample database. Unknown sample IDs must be less than or equal to 12 alpha-numeric characters. Any other sample that shouldn't be included into either database must have an ID preceded by '#'. There is a maximum of 50 analyses. Use <F4> "Choices" for selection of sample 'Type'. However, 24 unknowns to a set is recommended. Analyze a reference standard after every 6 unknown samples. CA50 and CA100 are used to calculate interferences on Co and Ni and should be analyzed at the end of the set. AS Pos. is the autosampler tray position; any tube position can be assigned.

Open file to store data:

[REPORTS]

Summary to file

To file - MYDATA.PRN

Set-up calibration file:

[CALIBRATION]

[SETUP CALIBRATION]

[FILE]-new

Change curve style using <F4> to 'linear through zero' for all isotopes.

[File]-Save as, choose calibration file name, For example, 'MYDATA'

[File]-close

* Insure the following:

Datafile should be MYDATA

Parameter set should be 'qa'

Calibration file should be MYDATA

Report file should be MYDATA.PRN

Load samples into tray.

Move sipper to wash station shift<F10>.

Connect sipper to peristaltic pump.

Minimize reflected RF power if needed.

Move cursor to top of analysis table, for example, BLANK.

Shift<F12> Analyze to end.

Postanalysis

Data can be reviewed through <Reports> <View>; select report.

<F3> close application, save calibration.

<APPLICATIONS>

<EXIT TO XENIX>

At login enter 'vpix'; the system is in the DOS environment.

Move to drive D:.

Change directory (cd) to instr\elan\data\reports.

The path should now be: u:\instr\elan\data\reports.

Make directory (md) MYDATA on A:.

Copy MYDATA.PRN to drive A:\MYDATA using DOS copy command.

Change directory to instr\elan\data\datasets.

Copy contents of directory using: xcopy MYDATA a:\MYDATA

Check that the files are on A floppy-disk drive

Execute 'exitvpix'

The system is now in the UNIX environment

Login as 'elan'

Data Processing

Process the data using program icpms.exe (for example c:\fortran and on the ICP-MS IBM in directory u:\instr\elan\data\reports). The calcium concentrations from the ICP-AES are needed for the samples being processed. First copy MYDATA.PRN into the working directory. Then execute ICPMS. Enter the calcium values for each sample. Four files will be generated MYDATA.TXT (text file for printout), MYDATA.MS (unknown samples database file), MYDATA.QCM (QC database file), and MYDATA.ARC (archive file). Copy all the MYDATA files to a floppy disk. A printout of the results (MYDATA.TXT) may be obtained using word-processor software.

Shutdown

Move sipper to load position shift<F9>

Close application <F3>

<APPLICATIONS>

<SHUTDOWN>, ok

Push 'Operation' button on MS to turn off plasma.

Turn-off peristaltic pump; remove tubing.

Turn-off monitor, computer, and autosampler.

Turn-off mass-flow controller.

Reset input power on match box to zero; move stage back.

Reset alarm on RF generator to zero, switch 'reflected' to off.

Close argon valve.

Cryoclean

(once a week for 4 hrs.)

<UTILITIES>

<CONFIGURATION>

<Windows> select Cryoclean

Set day and time to come on. <Schedule>

Leave computer on.