Optical Emission Inductively Coupled Plasma in Environmental Analysis

Mark E. Tatro

Spectra Spectroscopy & Chromatography Specialists, Inc., Warwick, USA

The ability of the ICP/AES (inductively coupled plasma/ atomic emission spectroscopy) system to perform multielement trace metal analysis of environmental samples provided commercial laboratories with the needed incentive to enter into the business of trace metal analysis. Previously, trace metals were typically analyzed using colorimetric techniques, which were both cumbersome and subject to interferences, or flame atomic absorption techniques, which although almost interference free, were labor intensive owing to their one element at a time analytical mode. Even the furnace atomic absorption technique, for years the standard bearer of low-level trace metal analysis, is giving way to axial viewed ICP/AES techniques.

Taking the USEPA (United States Environmental Protection Agency) SW-846 solid waste analysis manual as an example, this article reviews the methods used for the preparation of samples and the ICP/AES analysis of the prepared samples for trace metals in environmental matrices. The review includes a detailed overview of the quality control (QC) requirements for environmental ICP/AES analysis.

1 INTRODUCTION

Philosophers tell us that when we look back at our life's journey, the events that we viewed as a series of random unconnected acts when we were living them became instead a path that has cohesion and rationality. Such has been the history of ICP/AES for environmental analysis. This author remembers well the pre-ICP (inductively coupled plasma) days when to perform multielement analysis we relied on flame atomic absorption spectrometers which required the use of a different hollow cathode lamp and in some cases a different burner head for the analysis of each element.

Environmental applications were the driving force for the development of ICP instrumentation. In 1975, under contract to the USEPA, Royce Winge and Velmer Fassel[1] of Ames Laboratory reported on the development of ICP/AES for the simultaneous determination of trace element pollutants in water. The USEPA established its first official ICP/AES method for wastewater in 1979 as Method 200.7.[2]

In the 1980s, the decade of ICP, the USEPA approved ICP/AES for the following programs: National Pollutant Discharge Elimination System (NPDES); Safe Drinking Water Act (SDWA); Contract Laboratory Program (CLP); and Resource Conservation and Recovery Act (RCRA). An overview of the USEPA approved methods for ICP/AES can be found in the *Code of Federal Regulations* (40 CFR, Parts 136 and 141) and in the *Guide to Environmental Analytical Methods*.[3]

This article will expand on the USEPA programs listed above and how they affected the growth of ICP/AES for environmental analysis.

2 INDUCTIVELY COUPLED PLASMA DESIGNS

ICP/AES gained a strong foothold in environmental laboratories in the 1980s and 1990s due in part to the advantages over its predecessor flame atomic absorption spectroscopy listed here:

- multielement analysis capability
- large dynamic linear range
- reduction of matrix interferences

- improved detection limits for refractory elements
- enhancement of productivity.

The early ICP/AES designs of the 1980s that were approved for environmental analysis were of two types: simultaneous and sequential spectrometers with radial viewed torches.[4] The use of the radial viewed plasma results in a shortened path length which put the detection limit above the USEPA required detection limits for elements such as arsenic, lead, selenium and thallium. For these elements, the USEPA usually required the use of a heated graphite atomizer (HGA).[5]

Later ICP/AES designs of the 1990s approved for environmental analyses were axial viewed simultaneous and sequential spectrometers.[6] The use of the axial view of the plasma results in a longer path length that greatly improved detection limits and nearly eliminated the need for the use of the HGA to meet the USEPA detection requirements.[7]

Finally, ICP/AES spectrometers that could be programmed for both radial and axial view became the state-of-the-art where the less sensitive radial view was preferred for the higher concentration elements such as aluminum, calcium, iron, magnesium, potassium and sodium in environmental samples while the more sensitive axial view was preferred for the lower concentration elements such as the transition series.[8]

3 ENVIRONMENTAL SAMPLE PREPARATION FOR INDUCTIVELY COUPLED PLASMA/ATOMIC EMISSION SPECTROSCOPY ANALYSIS

3.1 Sources of Information

Sample preparation methods for ICP analysis of trace metals can be found in the following sources:

- The USEPA's Office of Solid Waste prepares and publishes the *SW-846* manuals for the analysis of groundwater, extracts, industrial wastes, soils, sludges, sediments, and solid wastes as dictated by the RCRA.[9]
- The American Public Health Association, the American Water Works Association and the Water Environment Federation jointly prepare and publish the *Standard Methods* manual for the analysis of drinking water and wastewater.[10]
- The USEPA's Office of Research and Development prepares and publishes its *Methods for the Determination of Metals in Environmental Samples* for the analysis of drinking water, surface water, saline and industrial and domestic wastes.[11]

- More recently, the USEPA published its *Methods for the Determination of Metals in Environmental Samples* Supplement I that updates sample preparation methods.[12]
- The USEPA's Superfund program prepares and publishes its *Contract Laboratory Program* manual for the analysis of wastewater and solid waste.[13]

The following method requirements are taken from the SW-846 manuals to provide the reader with an example of what sample preparation for ICP analysis entails. A compilation of approved methods of ICP sample preparation is presented in Table 1.

The sample introduction for ICP environmental applications requires that samples be in a liquid form so as to be aspirated through a nebulizer and that suspended solids be removed to prevent clogging of the nebulizer. Therefore, solid samples such as soils and sludges must first be acid digested to extract the metals of interest from the solids, and the resulting digestate must be filtered, centrifuged or allowed to sit to remove the suspended solids prior to analysis. Drinking water with a turbidity greater than 1 NTU (normal turbidity unit) must also be acid digested followed by the removal of suspended solids prior to analysis.

3.2 Hot Plate Digestions

The acid digestion of waters and solids, employing nitric and hydrochloric acids, can be effected by either hot plate (or hot block) methods or microwave methods. The hot plate methods for the preparation of waters can be quite confusing as they are subcategorized as being either "total" or "total recoverable" – or referred to by some as "hard" and "soft" respectively – where the "total" digestion is more rigorous than the "total recoverable" method. An example of a hot plate "total" digestion for wastewater is the SW-846 method 3010A and an example of a hot plate "total recoverable" method for wastewater is the SW-846 method 3005A. An example of a hot plate digestion for solids is SW-846 3050B.

3.3 Microwave Digestions

Microwave digestion methods are approved by the USEPA using either closed-vessel or open-vessel microwave digestion systems. Examples of closed-vessel microwave methods for wastewaters and solids are the SW-846 methods 3015A and 3051A, respectively. An example of an open-vessel microwave method is SW-846 method 3050B. Finally, SW-846 method 3052, a closed-vessel microwave method, which employs hydrofluoric acid for the preparation of siliceous and organic based matrices, is the only truly "total" digestion approved by the USEPA in that all suspended solids are solubilized.

Table 1 Digestion methods for environmental ICP/AES analysis

Method	Matrix	Reagents	Digestion type	Ref.
3005A	Water	HNO_3/HCl	Total recoverable	9
3010A	Water	HNO_3/HCl	Total	9
3015A	Water	HNO_3/HCl	Microwave	9
3031	Oils	Various	Total	9
3040A	Oils	Organic solvent	Dissolution	9
3050B	Soil	$HNO_3/H_2O_2/HCl$	Total recoverable	9
3050B	Soil	$HNO_3/H_2O_2/HCl$	Microwave	9
3051A	Soil	HNO_3/HCl	Microwave	9
3052	Silicates	$HNO_3/H_2O_2/HCl/HF$	Microwave	9
3030E	Water	HNO_3	Total	10
3030F(a)	Water	HNO_3/HCl	Total	10
3030F(b)	Water	HNO_3/HCl	Total recoverable	10
4.1.3	Water	HNO_3/HCl	Total	11
4.1.4	Water	HNO_3/HCl	Total recoverable	11
200.2	Water/soil	HNO_3/HCl	Total recoverable	12
ILMO4.0	Water	HNO_3/HCl	Total recoverable	13
ILMO4.0	Soil	$HNO_3/H_2O_2/HCl$	Total recoverable	13
200.7	Water/soil	HNO_3/HCl	Total recoverable	14
200.15	Water	HNO_3/HCl	Total recoverable	19

4 ENVIRONMENTAL INDUCTIVELY COUPLED PLASMA/ATOMIC EMISSION SPECTROSCOPY METHODS OF ANALYSIS

4.1 Sources of Methods

The most used ICP methods of environmental analysis are the USEPA's Office of Research and Development method 200.7 revision 4.4[14] and the USEPA's Office of Solid Waste SW-846 method 6010B.[9] Other environmental ICP methods of analysis which are similar to method 6010B include the Standard Methods method 3120B,[10] the CLP[13] and the Air Force Center for Environmental Excellence (AFCEE) at http://www.afcee.brooks.af.mil/index.html.

The USEPA also approves the use of its method 200.15 for drinking water analysis.[15] This method employs an ultrasonic nebulizer on the front end of an ICP/AES system to provide the better detection limits required for drinking water analysis. It is important to note that the USEPA does not yet approve ICP/AES, with or without ultrasonic nebulization, for the analysis of Pb, Sb, Se and Tl in drinking water.

The SW-846 method 6010B will be used here to provide an example of a typical environmental ICP method. For a comparison of various environmental ICP methods see Wagner.[3]

4.2 Recommended Inductively Coupled Plasma/Atomic Emission Spectroscopy Emission Lines

Table 2, taken from method 6010B, documents the suggested ICP emission line of choice and the estimated

IDL for a radial viewed plasma. Some programs such as the CLP publish Contract Required Detection Limits (CRDLs) that must be met by the instrument of choice (see Table 3). The CRDLs for As, Pb, Se and Tl required by the CLP's Statement of Work ILMO4.0 are 10, 3, 5 and 10, respectively. A radial viewed ICP does not meet these required detection limits. However, an axial viewed ICP will meet these required detection limits and, therefore, has become the instrument of choice for environmental analysis.

4.3 Compensating for Interferences

ICP emission suffers from spectral interferences and the analyst must document that these interferences have been eliminated. The two most common interferences experienced in environmental ICP analysis are (1) baseline shift caused mainly by high concentrations of Ca and Mg in samples and due to stray light, and (2) direct spectral overlap due to an emission line from an element in the sample that falls at or near the analyte wavelength and causes a false analyte concentration. Figure 1 shows the effect of both types of interference on the Sb 206.833 nm emission line for an axial view ICP. The calibration standard of 1000-ppb Sb (———) and the calibration blank (- - - -) are superimposed on the graphic that also displays the emission signal for an interference check standard (ICS[A]) with major elements only (·········) which contains 500-ppm Al, Ca, Mg and 200-ppm Fe as well as the emission signal for a standard that contains 10-ppm Cr, Mn and V (· · · ·).

If left unchecked the ICS[A] would give a false positive reading of approximately 800-ppb Sb. To prevent this,

Table 2 Recommended wavelengths and estimated instrumental detection limits (IDLs) for radial view ICP/AES[9]

Element	Wavelength (nm)	Estimated IDL ($\mu g\,L^{-1}$)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678×2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227×2	17
Molybdenum	202.030	5.3
Nickel	231.604×2	10
Phosphorus	213.618	51
Potassium	766.491	_[a]
Selenium	196.026	50
Silicon	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980×2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856×2	1.2

[a] Detection limit subject to plasma conditions.

Table 3 The CLP inorganic target analyte list[13]

Analyte	CRDL ($\mu g\,L^{-1}$)	Analyte	CRDL ($\mu g\,L^{-1}$)
Aluminum	200	Magnesium	5000
Antimony	60	Manganese	15
Arsenic	10	Mercury	0.2
Barium	200	Nickel	40
Beryllium	5	Potassium	5000
Cadmium	5	Selenium	5
Calcium	5000	Silver	10
Chromium	10	Sodium	5000
Cobalt	50	Thallium	10
Copper	25	Vanadium	50
Iron	100	Zinc	10
Lead	3		

a background correction point is programmed slightly to the left of the Sb calibration standard peak (L). During analysis the emission at the background correction point wavelength is subtracted from the emission at the
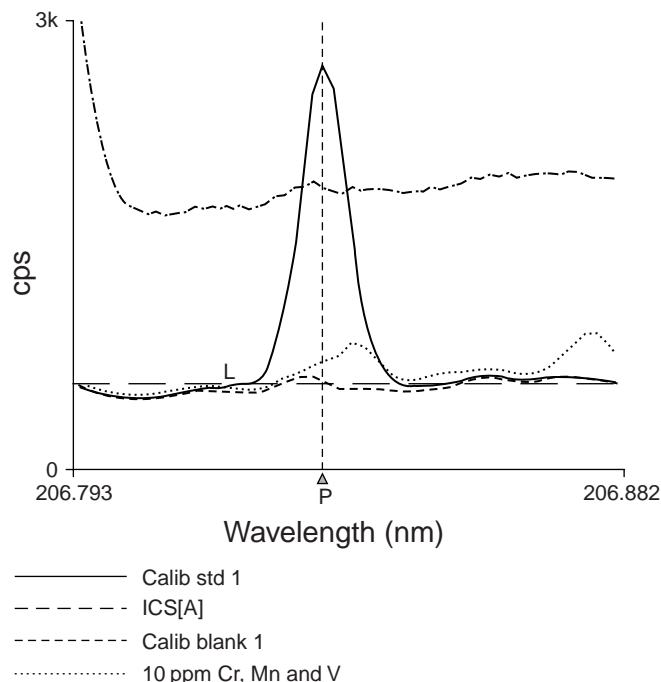

Figure 1 ICP/AES spectral overlays of the antimony 206.833-nm emission line (———) and a blank (- - - -) in the presence of an ICS[A] (-·-·-·-) and a mixed standard of chromium, manganese and vanadium (· · · ·). The overlays are used to set the background correction position and to verify if interelement correction factors (IECs) are required.

206.833-nm peak wavelength which effectively reduces the reading of the ICS[A] to less than detectable.

Referring again to Figure 1, the background correction point will not reduce the reading from the 10-ppm Cr, Mn, V standard since there is a false peak for Sb arising from one of the three elements in this standard (in this case the interference is due to Cr). To correct for this direct spectral overlap an IEC is required and must be documented.

Other interferences normally encountered in environmental ICP analysis are physical or matrix interferences caused by differences in viscosity or the amount of dissolved solids in samples, compared with standards. To reduce matrix interferences, analysts are required to prepare all standards and QC samples in the same acid matrix that exists for the digested samples. As a further control, analysts should use an internal standard such as Sc or Y to compensate for physical interferences.

4.4 Quality Control Protocols

After optimizing the instrument according to the manufacturer's specifications, the analyst is required to analyze a number of QC samples throughout the run where there are decisions to be made based on a window of acceptance for each QC sample analyzed.

The concept of the sample batch is used to describe the number of samples (typically a maximum of 20 samples) that are digested prior to ICP analysis and that are accompanied by QC samples that are also digested. The failure of the digested QC samples (see below) to meet acceptance criteria requires that the samples be redigested.

The complete list of the SW-846 method 6010B required QC samples is given in the following sections.

4.4.1 Initial Calibration

For SW-846 method 6010B, calibration of the ICP/AES requires one calibration standard within the linear range and one calibration blank.

4.4.2 Initial Calibration Verification Standard

This standard is prepared from a source different from the source used for the calibration of the ICP. The concentrations of the elements should be at a level that is 50% of the concentrations in the calibration standard. The initial calibration verification (ICV) standard is analyzed after initial calibration of the ICP to verify the calibration curve and must fall within an error of ±10% of the true value. Any analyte(s) that fails must be reanalyzed.

4.4.3 Continuing Calibration Verification Standard

This is the same as the ICV but analyzed after every ten samples and at the end of the run to monitor drift. If the continuing calibration verification (CCV) standard falls outside the error window of ±10%, then the ten samples preceding the failed CCV must be reanalyzed for the failed analyte(s).

4.4.4 Initial Calibration Blank

This contains the matrix acids and is analyzed after the ICV to monitor contamination and memory effects. If the ICB (initial calibration blank) is greater than three times the IDL the instrument must be recalibrated for the failed analyte(s).

4.4.5 Continuing Calibration Blank

This is the same as the ICB but analyzed after each CCV. If the CCB (continuing calibration blank) is greater than three times the IDL, then the ten previous samples must be reanalyzed for the failed analyte(s). However, if any of the ten previous samples are greater than ten times the failed CCB, then these sample(s) do not have to be reanalyzed.

4.4.6 Method Blank

This blank is carried through the entire sample preparation process. Although method 6010B does not provide a definitive QC window, laboratories usually assign the same criteria for the MB (method blank) as for the CCB. In other words, if the MB is greater than three times the IDL, then the samples must be redigested for the failed analyte(s) except for those samples that are more than ten times the failed MB.

4.4.7 Interference Check Standard

This standard contains 500-ppm Al, Ca, Mg, 200-ppm Fe and either 500 or 1000 ppb of all the analytes. The normal nomenclature used for this standard refers to the solution containing the major elements only (Al, Ca, Fe and Mg) as ICS[A]; the solution containing the 500 or 1000-ppb analytes only as ICS[B]; and, the combination of the two solutions as ICS[AB]. The ICS[AB] is used to verify that the background correction points and the IEC values are programmed correctly. Any analyte(s) that falls outside the error window of ±20% must be reanalyzed.

4.4.8 Matrix Spike/Matrix Spike Duplicate

One duplicate sample is spiked with a known concentration of analytes and is carried through the entire sample preparation process. A separate MS/MSD (matrix spike/matrix spike duplicate) must be prepared for waters, soils, and extracts. The relative percent difference (RPD) of the MSD must fall within ±20% error and the spike recovery must be within ±25% error.

4.4.9 Additional Quality Control

In the event that the matrix spike fails to fall within the allowed 75–125% recovery limits, the analyst must perform (1) a dilution test, and (2) a postdigestion spike addition.

1. Dilution test – a 1:5 dilution of the sample is prepared only if the analyte concentration is greater than ten times the IDL after dilution. The diluted concentration must agree with the undiluted concentration within ±10%.
2. Postdigestion spike addition – a spike containing the analytes at concentration between 10 to 100 times the IDL is added to the digested sample. The spike recovery must be within 75–125%.

4.4.10 Preanalysis Quality Control

Prior to any analysis, the following data must be gathered for each ICP/AES emission line:

- linear dynamic range
- method detection limits
- IDLs

Table 4 SW-846 method 6010B ICP/AES run log

Sample	QC error limits
Calibration blank	
Calibration standard	
ICV standard	±10%
ICV blank	<3 × IDL
ICS[A]	±20%
MB	<3 × IDL
Sample 1	
Sample 1 + MS	±25%
Sample 1 + MSD	±20% RPD
Sample 2	
Sample 3	
Sample 4	
Sample 5	
Sample 6	
CCV standard	±10%
CCV blank	<3 × IDL
Sample 7	
Sample 8	
Sample 9	
Sample 10	
CCV standard	±10%
CCV blank	<3 × IDL

- IECs
- background correction points.

A typical run log for ICP/AES analysis that follows the SW-846 method 6010B is shown in Table 4.

ACKNOWLEDGMENTS

ABBREVIATIONS AND ACRONYMS

AFCEE	Air Force Center for Environmental Excellence
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CRDL	Contract Required Detection Limit
HGA	Heated Graphite Atomizer
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP/AES	Inductively Coupled Plasma/ Atomic Emission Spectroscopy
ICS	Interference Check Standard
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
IEC	Interelement Correction Factor
MB	Method Blank
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NPDES	National Pollutant Discharge Elimination System
NTU	Normal Turbidity Unit
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RPD	Relative Percent Difference
SDWA	Safe Drinking Water Act
USEPA	United States Environmental Protection Agency

RELATED ARTICLES

Environment: Water and Waste **(Volume 3)**
Environmental Analysis of Water and Waste: Introduction • Detection and Quantification of Environmental Pollutants • Flame and Graphite Furnace Atomic Absorption Spectrometry in Environmental Analysis • Heavy Metals Analysis in Seawater and Brines • Inductively Coupled Plasma Mass Spectrometry in Environmental Analysis • Industrial Waste Dumps, Sampling and Analysis • Inorganic Environmental Analysis by Electrochemical Methods

Environment: Water and Waste cont'd **(Volume 4)**
Quality Assurance in Environmental Analysis • Sample Preparation for Environmental Analysis in Solids (Soils, Sediments, and Sludges) • Sample Preparation Techniques for Elemental Analysis in Aqueous Matrices

Atomic Spectroscopy **(Volume 11)**
Atomic Spectroscopy: Introduction • Inductively Coupled Plasma/Optical Emission Spectrometry

General Articles **(Volume 15)**
Analytical Problem Solving: Selection of Analytical Methods • Quality Assurance in Analytical Chemistry • Quantitative Spectroscopic Calibration

REFERENCES

1. R.K. Winge, V.A. Fassel, R.N. Kniseley, E. Kalb, W.J. Haas, Jr, 'Determination of Trace Elements in Soft, Hard, and Saline Waters by the ICP Multi-element Atomic

Emission Spectroscopic Technique', *Spectrochim. Acta, Part B*, **32**, 327 (1977).

2. 'Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes – Method 200.7', in Methods for the Determination of Metals in Environmental Samples – Supplement 1, USEPA Office of Research and Development, EPA/600/R-94/111, 1994.

3. R.E. Wagner (ed.), *Guide to Environmental Analytical Methods*, 4th edition, Genium Publishing Corporation, Schenectady, NY, 1998.

4. G.A. Meyer, 'A Review of Sequential and Simultaneous ICP Spectrometers for Trace Metal Analysis', *Anal. Chem.*, **59**, 1345A – 1354A (1987).

5. V.A. Letourneau, B.M. Joshi, L.C. Butler, 'Comparison of Furnace AA Spectral Interferences between a Continuum and Zeeman Background Correction Spectrometer', *At. Spectrosc.*, **8**(5), 149 (1987).

6. D.E. Dobb, J. Heitschmidt, T.M. Hall, 'A Comparison of Radial and Axial-viewed ICP/AES Instruments for the Determination of As, Ag, Cd, Pb, Se and Tl in Environmental Samples', *The Pittsburgh Conference*, Chicago, IL, March 5, Paper 238P, 1996.

7. M.E. Tatro, L.C. Camp, R.K. Christenberry, 'Analysis of As, Pb, Se and Tl in Solid Waste using a Simultaneous Trace Analyzer ICP', *Spectroscopy*, **9**(7), 36 (1994).

8. M. Duffy, R. Thomas, 'Benefits of a Dual-view ICP/OES for the Determination of B, P and S in Low Alloy Steels', *At. Spectrosc.*, **17**(3), 128 (1996).

9. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Vol. 1, Government Printing Office, Washington, DC, December 1996.

10. Standard Methods for the Examination of Water and Wastewater, 20th edition, part 3000, American Public Health Association, Washington, DC, 1998.

11. EPA/600/4-79-020, Methods for Chemical Analysis of Water and Wastes, USEPA, Office of Research and Development, Washington, DC, 1983.

12. EPA/600/R-94/111, Method 200.2 Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements in Water and Wastes by Inductively Coupled Plasma/Atomic Emission Spectrometry, revision 4.4 in Methods for the Determination of Metals in Environmental Samples – Supplement I. USEPA Office of Research and Development, May 1994.

13. USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Document No. ILM04.0, EPA-540/R-95/121 (1995) US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Exhibit D, Sec. III, p. D-5, Government Printing Office, Washington, DC.

14. EPA/600/R-94/111, Method 200.7 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma/Atomic Emission Spectrometry, revision 4.4 in Methods for the Determination of Metals in Environmental Samples – Supplement I. USEPA Office of Research and Development, May 1994.

15. EPA/600/R-94/111, Method 200.15 Determination of Metals and Trace Elements in Water by Ultrasonic Nebulization Inductively Coupled Plasma/Atomic Emission Spectrometry, revision 1.2 in Methods for the Determination of Metals in Environmental Samples – Supplement I. USEPA Office of Research and Development. May 1994.