

Atomic Absorption

Author

Praveen Sarojam, Ph.D.

PerkinElmer, Inc.
Shelton, CT USA

Analysis of Essential, Trace and Heavy Metals in Drinking Water by Flame AA and Graphite Furnace AA

Introduction

Heavy metals are among one of the significant pollutants of freshwater, with the development of mining, smelting and other industrial activities¹. Heavy metal pollution not only affects the productivity of crops, but also the quality of the atmosphere and water bodies and threatens the health and life of animals

and human beings by way of the food chain². Essential metals (Ca, K, Mg, Na, etc.) are required for the routine functioning of the human body. Presence of certain trace metals (Ba, Cu, Fe, Mn, Ni, Se, Zn etc.) at catalytic amounts, such as copper and zinc, based on their role as metalloenzymes and as a cofactor of a large number of enzymes, are required for living organisms and their normal physiological activities. A high concentration of Cu had been correlated with liver damage. Zinc may produce adverse nutrient interactions with copper. Also, Zn reduces immune function and levels of high density lipoproteins⁴. Heavy metals (As, Ag, Cd, Pb, etc.) are not required for routine functioning of the human body. These metals are toxic even at low concentrations. The pollution caused by heavy metals is a long-term and irreversible process. Even though some of the metals act as micronutrients at small concentrations, their accumulation in higher concentration becomes toxic to most life forms^{3,5}.

Drinking water from any source such as a private well, public water system, river or lake is a source of environmental contamination. Usually, the natural contamination of heavy metals originates from weathering of minerals, rocks and aquatic environments which results in the entry of heavy metals into water bodies⁶. Disposal of industrial effluents, wastes (domestic and industrial) such as sewage sludge, and mining effluents are other reasons for contamination. Many of the metals are retained in the surface water and soil and do not readily leach out—causing accumulation that may ultimately pose a threat to humans, animals, plants and microbes. Still, there is a pressing need to deal with excess metals present in water bodies to protect the environment from metal contaminants^{2,3}. The U.S. EPA has set maximum contaminant levels (MCL) for various metal ions (See Table 1) in drinking water. This means that public water supplies are monitored for these metals regularly. Private drinking water systems are not monitored and it is up to the owner or consumer to test and treat their water.

Markets today are flooded with many choices of bottled drinking waters. There is a possibility branded names may be counterfeited and because of dubious preparation methods, bottled waters may be contaminated at the source itself. Hence, the bottled waters available in the market also need to be monitored routinely for trace and ultra trace levels of metal impurities.

Atomic spectroscopy techniques such as atomic absorption (flame and furnace), inductively coupled plasma optical emission (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) have been used for the determination of essential, trace and toxic heavy metals in drinking waters. In some cases, the capabilities of the techniques overlap and several are suitable for a particular analytical scenario. This study examines the suitability of flame and furnace atomic absorption spectroscopy for the determination of essential, trace and toxic heavy metals in drinking water. It is prudent to choose a technique with a detection limit approximately ten times below the MCL for the most reliable answer at the decision making point. The validation of the developed method has been done by analyzing NIST® certified reference material for drinking water (NIST® 1643e). The performance of the developed method was further assessed by spiking the samples and also by analyzing QC samples.

Table 1. Drinking Water Regulatory Limits and Instrument Detection Limits (IDLs) for Atomic Absorption Spectrophotometers⁴.

Element	U.S. MCL (µg/L)	European Union (µg/L)	WHO (µg/L)	FLAA IDL (µg/L)	GFAA IDL (µg/L)
Sb	6	5	5	45	0.05
As	10	5	5	150	0.05
Ba	2000	–	700		
Be	4	–	–		
Cd	5	5	3	0.8	0.1
Cr	100	50	50	3	0.004
Cu	1300	2000	1000	1.5	0.014
Pb	15	10	10	15	0.05
Ni	100	20	20	6	0.07
Se	50	10	10	100	0.05
Tl	2	–	–		
Al*	50			45	0.1
Fe*	300			5	0.1
Zn*	5000			1.5	0.02
Na*	20 (mg/L)			0.3	0.005
Mg*	50 (mg/L)			0.15	0.004
Ca*	250 (mg/L)			1.5	0.01
K*	12 (mg/L)			3	0.005

* Secondary drinking water contaminant

Nine elements were determined by graphite furnace atomic absorption (GFAA) and eleven elements were determined by flame atomic absorption (FLAA) in a variety of drinking water and bottled water samples.

Experimental

Instrumentation

The measurements were performed using the PerkinElmer® AAnalyst™ 800 atomic absorption spectrophotometer (PerkinElmer, Inc., Shelton, CT, USA) (see Figure 1) equipped with WinLab32™ for AA, version 6.5 software, which features all the tools to analyze samples, report and archive data and ensure regulatory compliance. PerkinElmer’s high-efficiency double-beam optical system and solid-state detector provide

outstanding signal-to-noise ratios and the transversely heated graphite atomizer (THGA) tube design along with the Zeeman background correction technique eliminate most interferences. A PerkinElmer high sensitivity nebulizer assembly with Pt/Ir capillary was used for all flame absorption measurements. A single slot 10 cm burner head was used for all air-acetylene elements and a 5 cm burner head was used for the nitrous oxide-acetylene elements.

All graphite furnace analyses were performed with Zeeman background correction. PerkinElmer's unique, transversely-heated graphite tube with integrated platform was used for all graphite furnace analysis. Analysis of As and Cd was done with THGA graphite tubes with end caps for higher sensitivity. EDL lamps were used whenever available. The AS 800 autosampler with a 148-position tray was used for furnace autosampling and polypropylene autosampler cups were used for sample handling.



Figure 1. PerkinElmer AAnalyst 800 atomic absorption spectrophotometer and THGA graphite tube with integrated platform.

Standards, Chemicals and Certified Reference Material

PerkinElmer single element calibration standards for atomic spectroscopy were used as the stock standards for preparing working and quality control standards. All the working standards were prepared daily in ASTM® Type 1 water (Millipore® filter system) and acidified with 1% Suprapur® nitric acid in polypropylene vials (Sarstedt®) on volume-by-volume dilution. Micropipettes (Eppendorf®, Germany) with disposable tips were used for pipetting solutions. High purity HNO₃ (Suprapur®, Merck®, Germany) was used for sample acidification. PerkinElmer matrix modifiers (Pd and Mg as nitrate) were used for graphite furnace AA analysis. Certified Reference Material (CRM) for water NIST® 1643e was used for validating the developed method.

Sample Preparation

Two well waters, one river, one lake and one ground water sample were collected. Also, five bottled water samples from reputed firms were directly purchased from the market. The mineral content was given by the manufacturer, in only one of the bottled waters purchased. The water was sampled in the morning, brought to the laboratory and after standing undisturbed overnight, was flushed into a plastic bottle containing 1% of Suprapur® nitric acid. Similarly, the bottled waters were poured into a 50 mL graduated polypropylene vial and 500 µL of nitric acid was added. Spiked samples were also prepared by adding known quantity of analyte ions to two representative drinking water samples (see Tables 1 and 2 for details).

For drinking water compliance monitoring, a "total" element determination (dissolved and suspended) is required. For the determination of trace and matrix elements in drinking water, samples are not filtered, but acidified with nitric acid to a pH <2. Preservation may be done at the time of collection or when returned to the laboratory, depending upon regulatory requirements.

Instrument Operating Conditions

The instrumental conditions for flame and furnace experiments are given in Tables 3 and 2, and the graphite furnace temperature programs are listed in Appendix I. A heated injection at 900 °C was used for all the experiments. Pyrolytically coated graphite tubes with integrated platforms were used. The autosampler cups were soaked in 20% nitric acid overnight to minimize sample contamination, and thoroughly rinsed with 0.5% HNO₃ acid before use. This will be a problem with aluminum, which is present in dust, paper towels and other common laboratory supplies. A 5 µL amount of matrix modifier containing 0.1% of Pd and 0.06% of Mg (as nitrate) was added automatically to each standard, sample and blank by the autosampler AS 800, an integral part of the AAnalyst 800. Several quality control checks were automatically performed by the software, as specified in the method. The calibration curve correlation coefficient was ensured to be better than 0.995 (see Appendix II and III).

Table 2. Operating Conditions of Graphite Furnace Analysis on the AAnalyst 800.

Element	Pb	Tl	Cd	Cr	Be	Sb	Se	Al	As
Wavelength (nm)	283.3	276.8	228.8	357.9	234.9	217.6	196	309.3	193.7
Slit (nm)	0.7	0.7	0.7	0.7	0.7	0.7	2.0	0.7	0.7
Mode	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG
Signal measurement	Peak area	Peak area	Peak area	Peak area	Peak area	Peak area	Peak Area	Peak area	Peak area
Calibration Equation	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.	Lin. cal. int.
Sample volume (µL)	20	20	20	20	20	20	20	20	20
Lamp	EDL	EDL	EDL	HCL	HCL	EDL	EDL	HCL	EDL
Lamp current (mA)	440	380	230	25	30	320	280	25	380
Standards (µg/L)	10, 25, 50	10, 25, 50	0.5, 1, 2	4, 12, 20	2, 6, 10	10, 25, 50	10, 25, 50	10, 25, 50	10, 25, 50
Spiked conc. (µg/L)	20	20	0.1	8	4	20	20	20	20

Table 3. Operating Conditions for the Flame Analysis with the AAnalyst 800.

Element	Ag	Cu	Fe	Mn	Ni	K	Na	Mg	Ca	Ba*	Zn
Wavelength (nm)	328.1	324.8	248.3	279.5	232	766.5	589	285.2	422.7	553.6	213.9
Slit (nm)	0.7	0.7	0.2	0.2	0.2	0.7	0.2	0.7	0.7	0.2	0.7
Mode	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA
Flame	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	Air-Ac	NO-Ac
Burner	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm	5 cm	10 cm
Calibration Equation	Lin. cal. Int.	Lin. cal. Int.	Lin. cal. Int.	Lin. cal. Int.	Lin. cal. Int.	Lin. thr' zero	Non lin. thr' zero	Non lin. thr' zero	Non lin. thr' zero	Non lin. thr' zero	Non lin. thr' zero
Lamp	HCL	HCL	HCL	HCL	HCL	HCL	HCL	HCL	HCL	HCL	HCL
Lamp current	10	15	30	20	25	12	8	6	10	25	15
Standards (µg/L)	50, 100, 200, 500	250, 500 1000, 2000 4000	250, 500 1000, 2000	100, 200 400, 1000	100, 200 500, 1000	500, 1000 2000, 4000	100, 250 500	250, 500 1000, 2000	500, 1000 2000, 4000	2500, 5000 10000, 20000	50, 100 1000, 2000
Spiked conc. (µg/L)	100	1000	1000	200	200	100	100	100	1000	5000	100

* Barium is analyzed using the nitrous oxide-acetylene flame.

Results and Discussion

The goal of the GFAA method development was to make the method most useful for routine drinking water analysis. The patented THGA tube used in the AAnalyst 800 provides a uniform temperature distribution along its entire length. This eliminates cooler temperatures at the tube ends and removes most interference. There is no re-condensation, carry-over and memory effect is eliminated. With the THGA tube design, accuracy and sample throughput are improved by reducing the need for the time-consuming standard additions technique. With the longitudinal Zeeman-effect background correction, the amount of light throughput is doubled by eliminating the need for a polarizer in the optical system. All other commercial Zeeman designs incorporate inefficient polarizers that reduce light throughput and diminish performance. With this unique design, the AAnalyst 800 provides the lowest detection limits available.

In conventional furnace systems, the heating rate during atomization depends on the input-line voltage. As voltage may vary from day to day, season to season or among laboratory locations, so may the heating rate. The high-performance AAnalyst 800 uses enhanced power control circuitry to maintain a uniform heating rate, irrespective of the location of the instrument, one can be sure that it provides outstanding, and consistent performance.

The accuracy of the developed method was tested by analyzing water Reference Material NIST® 1643e (supplied by National Institute of Standards and Technology, Gaithersburg, MD, USA). The results obtained are given in Table 4. The values obtained by the present method matched closely with the certified values. Two representative water samples, (river water and one bottled water) were spiked with known amounts of analytes and their recoveries were within 80-120% limits (see Table 5). The QC samples were prepared from multi-element quality control standards for ICP for different metal ions (Spex Certiprep® (New Jersey, USA).

Table 4. Analysis of NIST® 1643e with GFAA (Certified Reference Material Supplied by NIST®, USA).

Element	Certified Value (µg/L)	Measured Value (µg/L)	QC 1 Recovery (%)	QC 2 Recovery (%)
Cadmium	6.568 ±0.073	6.53 ±0.24	108	107
Selenium	11.97 ±0.14	11.7 ±0.22	105	103
Antimony	58.30 ±0.61	57.2 ±1.2	107	107
Beryllium	13.98 ±0.17	14.4 ±0.18	108	113
Arsenic	60.45 ±0.72	60.5 ±0.54	100	102
Aluminum	141.8 ±8.6	139.1 ±5.0	108	103
Lead	19.63 ±0.21	19.3 ±0.22	108	111
Chromium	20.40 ±0.24	20.8 ±0.24	86.1	98.9
Thallium	7.445 ±0.096	7.39 ±0.044	98.6	114

Table 5. Results of GFAA Analysis of Drinking and Bottled Waters (µg/L).

Elements	Pb	Tl	Cd	Cr	Be	Sb	Se	Al	As
Lake water	3.8	0.13	0.01	<DL	1.52	0.22	0.05	40.5	2.55
Well water I	5.4	0.35	0.27	<DL	1.52	<DL	<DL	30.9	<DL
Bottle water1	4.1	0.09	0.01	<DL	<DL	0.11	0.008	2.1	<DL
Ground water	5.8	0.08	0.01	<DL	<DL	0.12	0.009	58.4	0.33
Bottle water 2	4.9	0.13	0.002	<DL	1.02	0.08	<DL	1.1	<DL
Bottle water 3	5.0	0.14	<DL	<DL	1.53	0.02	0.08	0.12	<DL
Bottle water 4	8.1	0.11	0.005	<DL	0.91	0.4	<DL	2.2	<DL
Bottle water 5	4.6	0.10	<DL	<DL	1.52	0.68	0.11	3.7	<DL
River water	7.2	0.03	0.04	<DL	1.31	<DL	0.07	1174	0.13
Well water II	5.1	0.08	0.03	<DL	1.41	0.17	0.11	5.4	<DL
Spike (Bottled) (% recovery)	(98.6)	(93.0)	(102.7)	(99.4)	(101.9)	101	92.4	**	108
Spike (River) (% recovery)	(100.4)	(97.5)	(104.9)	(105.6)	(110)	104	99.4	**	110

**Native concentration too high for spiking

The GFAA results show that none of the water samples contain toxic metals above the U.S. MCL limits. Aluminum content was well above the U.S. MCL limit for the river water which shows that it is not suitable for drinking purposes.

The results for the flame analysis of the NIST® 1643e CRM are given in Table 6. Sensitivity and accuracy in flame AA are directly correlated to the optimization of the burner position as well as the gas flows. Careful optimization of these parameters, which are different for each element,

maximizes sensitivity and can significantly reduce or eliminate interferences. The unique computer-controlled, motorized burner system and gas controls allow precise, automated adjustments. Since WinLab32 software allows optimized burner position and gas flows to be stored with an element method, each element in a sequential multi-element run can be determined using its own optimized parameters. The measured results showed excellent agreement with the certified values. The average QC recovery was between 90-110%.

Table 6. Analysis of NIST® 1643e with FLAA (Certified Reference Material Supplied by NIST®, USA).

Element	Lowest STD	Absorbance for Lower STD	Certified Value($\mu\text{g/L}$)	Measured Results ($\mu\text{g/L}$)	QC Recovery (%)
Mn	100 ppb	0.009	38.97 \pm 0.45	41.5 \pm 5.3	107
Cu	250 ppb	0.025	22.76 \pm 0.31	26.6 \pm 1.4	104
Zn	500 ppb	0.022	78.5 \pm 2.2	76.0 \pm 3.6	99
Ni	100 ppb	0.006	62.41 \pm 0.69	78.1 \pm 18.8	104
Fe	250 ppb	0.008	98.1 \pm 1.4	91.0 \pm 3.55	102
Na	0.05 ppm	0.024	20740 \pm 260	21000 \pm 260	105
K	0.05 ppm	0.019	2034 \pm 29	(1970) \pm (78)	106
Mg	0.025 ppm	0.038	8037 \pm 98	(8100) \pm (122)	101
Ca	0.5 ppm	0.109	32300 \pm 1100	32500 \pm 380	104
Ba	2.5 ppm	0.029	544.2 \pm 5.8	557 \pm 8.6	101

Table 7 shows the results of the two spike recoveries (one with bottled water and the other with river water). See Tables 2 and 3 for spiked concentrations and two QC recovery studies for the flame analysis. Samples were diluted with 1% KCl for Ba and for Ca determination;

sample dilution was done with 1% Lanthanum in 1% HNO₃. In some cases, samples and the Certified Reference Material (NIST® 1643e) were diluted appropriately so that concentration of the analyte of interest would fall within the calibration concentration ranges.

Table 7. Results of Flame AA Analysis of Drinking and Bottled Waters (* $\mu\text{g/L}$, ** mg/L).

Elements	Ag	Cu*	Fe*	Mn*	Ni*	Zn**	K**	Na**	Mg**	Ca**	Ba**
Lake water	<DL	5.08	<DL	2.08	<DL	<DL	2	38.0	9.72	13.1	2.67
Well water I	<DL	7.98	43.6	3.68	<DL	628	0.7	39.9	8.18	123	2.92
Bottle water 1	<DL	0.103	<DL	<DL	<DL	8	2.12	25.3	4	9.02	3.03
Ground water	<DL	9.21	<DL	<DL	<DL	69	<DL	4.5	3.3	12.0	0.34
Bottle water 2	<DL	2.17	<DL	<DL	<DL	4	0.85	1.46	0.06	0.397	0.35
Bottle water 3	<DL	6.05	<DL	<DL	<DL	7	<DL	2.4	2.68	0.332	0.33
Bottle water 4	<DL	8.19	<DL	<DL	<DL	3	0.19	14.2	1.3	4.94	0.38
Bottle water 5	<DL	7.73	<DL	<DL	<DL	19	4.14	4.12	2.78	5.93	0.47
River water	<DL	9.40	472	<DL	<DL	7	1.02	79.4	7.8	3.64	0.53
Well water II	<DL	5.46	<DL	<DL	<DL	80	3.58	32.7	2.88	4.65	0.56
Spike (Bottled water) (% recovery)	96.7	100	105	106	103	99	92	-	-	-	84.6
Spike (River water) (% recovery)	107	103	103	98.3	86.4	98	96	-	-	-	81.44

The spike recoveries and QC recoveries are generally within 85-115%, as specified by EPA for post-digestion spikes. The flame analysis results show that most of the bottled water samples contain essential and trace metals below the U.S. MCL limits. But the content of sodium in river and

lake waters, well waters and in one of the bottled waters is above the U.S. MCL limit. This could be due to high sodium (NaCl) content in these waters. Hence they may require purification before they are used as drinking water.

Conclusion.

A method is developed for the determination of essential, trace and toxic metals in drinking water at regulatory levels. The procedure is used with good effect for the analysis of various metal ions in samples including river, lake, and well water and also for bottled waters with acceptable accuracy and precision. The metal contents at $\mu\text{g/L}$ levels were determined easily. The other main advantages of the method include simplicity, time savings and cost effectiveness. Flame and GFAA can be combined to provide a low cost system capable of monitoring drinking water at regulatory levels. The use of an autosampler facilitates the unattended operation of the instrument.

References

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Appendix I. Graphite Furnace Temperature Programs.

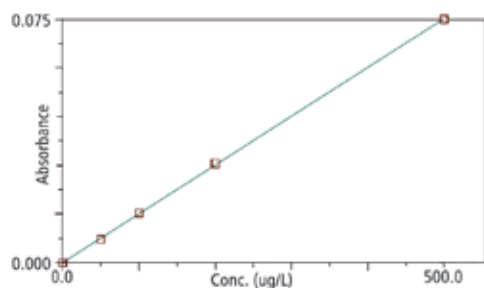
Element	Step	Temp. °C	Ramp Time (Sec)	Hold Time (Sec)	Internal Gas Flow (mL/min)	Gas Type
Se	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	1300	10	20	250	Argon
	4	1900	0	5	0	Argon
	5	2450	1	3	250	Argon
Cd	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	500	10	20	250	Argon
	4	1500	0	5	0	Argon
	5	2450	1	3	250	Argon
As	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	1200	10	20	250	Argon
	4	2000	0	5	0	Argon
	5	2450	1	3	250	Argon
Al	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	1200	10	20	250	Argon
	4	2300	0	5	0	Argon
	5	2450	1	3	250	Argon
Tl	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	700	10	20	250	Argon
	4	1600	0	5	0	Argon
	5	2450	1	3	250	Argon
Sb	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	1300	10	20	250	Argon
	4	1900	0	5	0	Argon
	5	2450	1	3	250	Argon
Pb	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	850	10	20	250	Argon
	4	1600	0	5	0	Argon
	5	2450	1	3	250	Argon

Appendix I continued.

Element	Step	Temp. °C	Ramp Time (Sec)	Hold Time (Sec)	Internal Gas Flow (mL/min)	Gas Type
Be	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	1500	10	20	250	Argon
	4	2300	0	5	0	Argon
	5	2450	1	3	250	Argon
Cr	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	1500	10	20	250	Argon
	4	2300	0	5	0	Argon
	5	2450	1	3	250	Argon

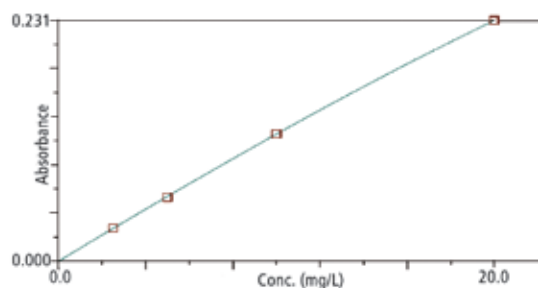
Appendix II. Calibration Graphs for Flame AA Analysis.

Ag 328.1



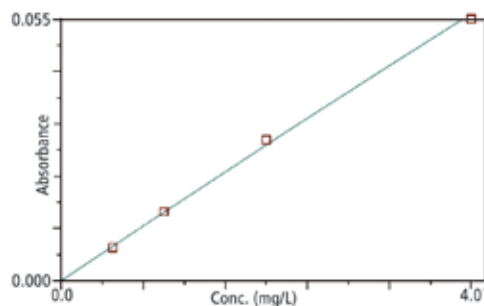
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Corr Coeff: 0.999947

Ba 553.6



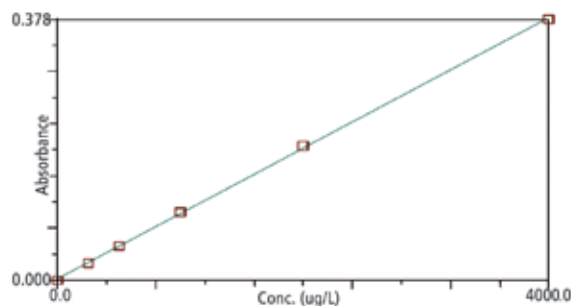
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Ca 422.7



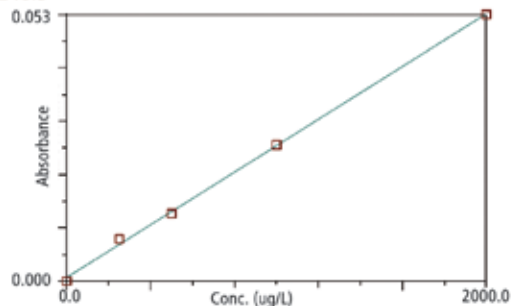
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Cu 324.8



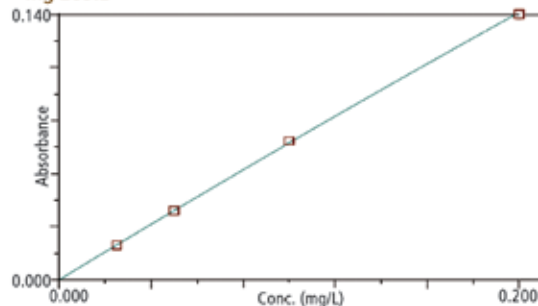
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Corr Coeff: 0.999877

Fe 248.3



Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999406

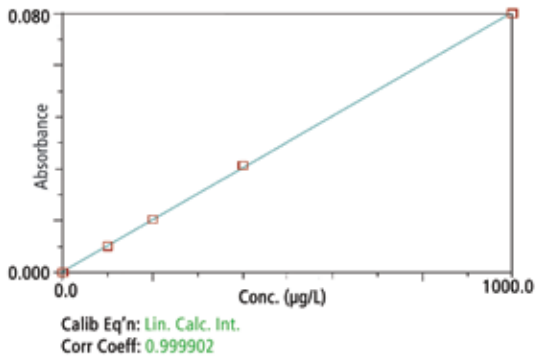
Mg 285.2



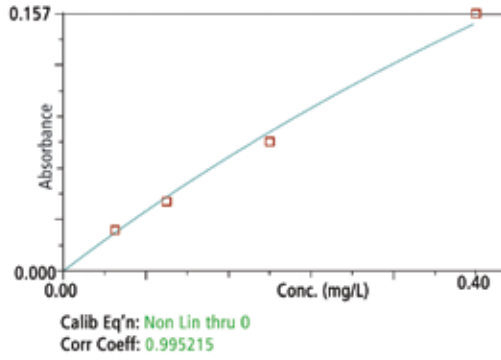
Calib Eq'n: Non Lin. Thru 0
Corr Coeff: 0.999878

Appendix II continued.

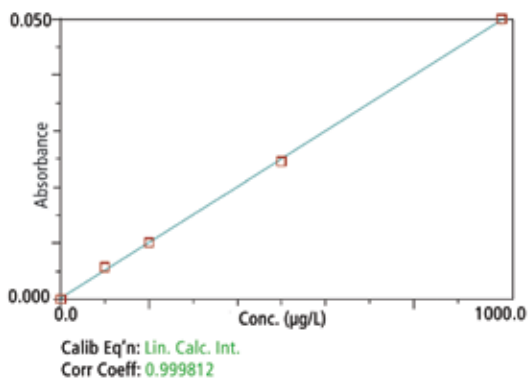
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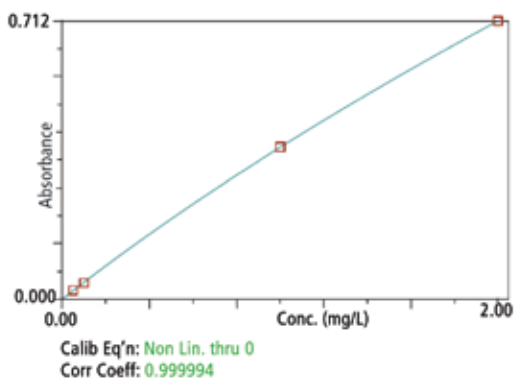
Na 589.0



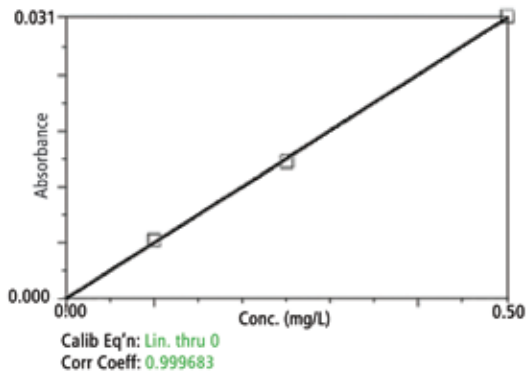
Ni 232.0



Zn 213.9

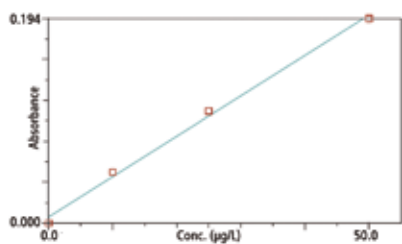


K 766.5



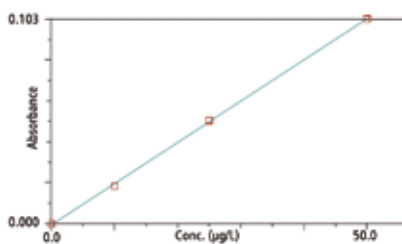
Appendix III. Calibration Graphs for Graphite Furnace AA Analysis.

Al 309.3



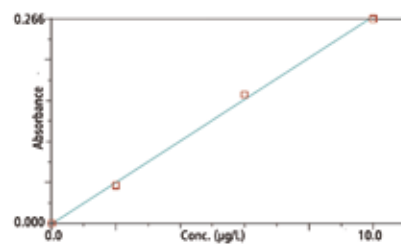
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.997979

As 193.7



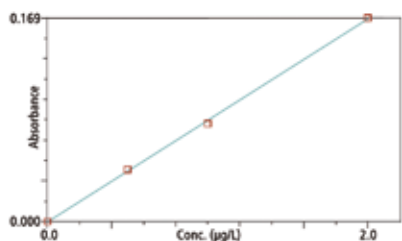
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999791

Be 234.9



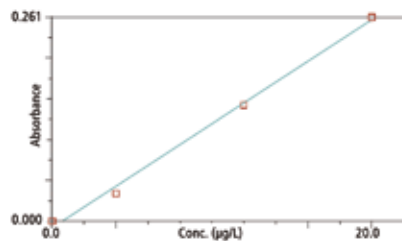
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999278

Cd 228.8



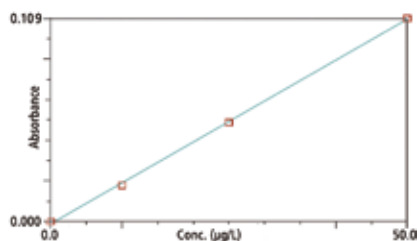
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999694

Cr 357.9



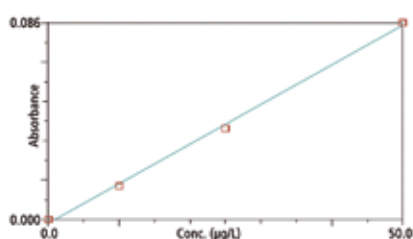
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.997842

Pb 283.3



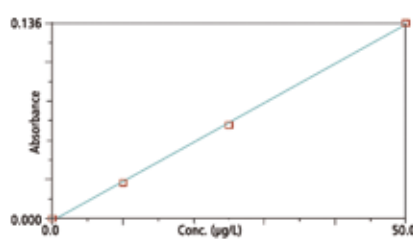
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999737

Sb 217.6



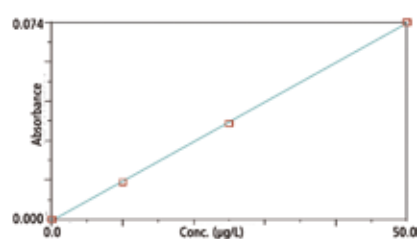
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999019

Se 196.0



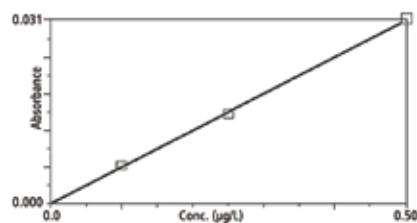
Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999630

Tl 276.8



Calib Eq'n: Lin. Calc. Int.
Corr Coeff: 0.999863

K 766.5



Calib Eq'n: Lin. thru 0
Corr Coeff: 0.999683