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Application News

No. ICP-004

Inductively Coupled Plasma Atomic Emission Spectrometry

Fast, Sensitive, and Cost-effective Analysis of Trace Metals in Water by EPA Method 200.7 Using the Shimadzu ICPE-9820

■ Introduction

The Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer is the ideal instrument for running EPA Method 200.7. The ICPE-9820 permits simultaneous analysis of all elements, at all wavelengths, allowing high-throughput analysis with little need for dilution. The large 1-inch CCD detector with over 1 million pixels measures 110,000 wavelengths. Overflow channels prevent blooming, providing more active surface area on the detector. Equipped with a mini-torch, the instrument can achieve excellent sensitivity while cutting argon consumption in half. The vacuum-sealed optical bench further reduces argon consumption and provides stable measurements down to 167 nm. The vertically orientated torch minimizes the adhesion of sample to the walls of the torch reducing clogging and memory affects. With dual view capabilities, the instrument automatically switches between axial and radial viewing to allow up to nine orders of magnitude measurement.

■ Procedure

EPA Method 200.7, *Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-Atomic Emission Spectrometry*, describes the procedure and requirements for multi-element determinations by Inductively Coupled Plasma – Atomic Emission Spectrophotometry (ICP-AES). The ICPE-9820 co-axial nebulizer and cyclone spray chamber transport a fine aerosol mist into the mini torch. A radio frequency inductively coupled plasma ionizes every element emitting element specific spectra. A diffraction grating disperses the spectra and a photosensitive detector measures the intensities of the spectral lines. Samples must be well mixed and homogenous. Digest solid samples or samples that contain undissolved material by gently refluxing with nitric and hydrochloric acids.

■ Instrumentation

All measurements were performed using the Shimadzu ICPE-9820 spectrometer equipped with a mini-torch, a cyclonic spray chamber, and a co-axial nebulizer. A 1-ppm Yttrium internal standard solution was mixed in line with all samples using the ASC-9800 auto-sampler, the internal standard addition kit, and the built-in peristaltic pump. Dual view optics obtain measurements in both the axial and radial viewing positions, enabling quantitation of a wide dynamic range. See Table 1 for the instrument parameters. Total Argon flow is 11.3 Liters per Minute (L/min) and the total read time is 180 seconds per sample for three replicates; only 33.9 liters of Argon is used per sample. This rapid analysis time and low argon usage greatly increases throughput and reduces the cost per analysis.

Table 1: Instrument Parameters

Parameter	Setting
Nebulizer type	Co-axial
Spray Chamber	Cyclone
Torch	mini
Plasma Gas Flow (L/min)	10.0
Aux Gas Flow (L/min)	0.6
Neb Gas Flow (L/min)	0.7
RF Power (watts)	1200
Read Time (s)	30 (axial), 30 (radial)
Replicates	3
Peak Processing	peak area
Calibration Type	Linear

■ Standard Prep and Calibration

The instrument was calibrated with standards purchased from Inorganic Ventures.[1] The stock solutions were diluted in 1% HNO3 and a multi-point calibration curve was created for each element. Yttrium was used as an internal standard.

Calibration Standard	Elements Included	Dilutions for working standards CAL 1	CAL 2	CAL 3	CAL 4
WW-CAL-1A	1000 ug/ml: As, Ca 500 ug/ml: Se 200 ug/ml: Cd, Cu, Mn 100 ug/ml: B, Ba, Sr 50 ug/ml: Ag	blank	1000 x	500 x	100 x
WW-CAL-2	2000 ug/ml: K 1000 ug/ml: Mo, Na, Ti 500 ug/ml: Li	blank	1000 x	500 x	100 x
WW-CAL-3	1000 ug/ml: P 200 ug/ml: Ce, Co, V	blank	1000 x	500 x	100 x
WW-CAL-4A	1000 ug/ml: Al 500 ug/ml: Cr, Zn 200 ug/ml: Hg	blank	1000 x	500 x	100 x
WW-CAL-4B	1000 ug/ml: SiO2 400 ug/ml: Sn	blank	1000 x	500 x	100 x
WW-CAL-5	1000 ug/ml: Fe, Mg, Pb 500 ug/ml: Tl 200 ug/ml: Ni 100 ug/ml: Be	blank	1000 x	500 x	100 x
CLPP-SPK-2	500 ug/ml: Sb	blank	1000 x	500 x	100 x

■ Results

To verify that the system was working correctly and suitable for the analyses, the IDLs and MDLs were determined. The IDLs were calculated using single-element standards. The MDLs were calculated following the procedure at 40 CFR Part 136, Appendix B. These results are listed in **Table 2**.

For the more sensitive elements, or elements that could exist in samples at higher concentrations, both the axial and radial results were recorded.

The concentration of certain elements can vary widely in environmental samples. Elements in high concentration can produce an interference, known as spectral overlap, which can result in false positives or false negatives for the elements at lower concentrations. For this reason, the spectrometer and software need to be able to compensate for these differences in concentration to accurately measure all analytes in the sample.

Inter-Element Corrections, or IEC, is the preferred method for dealing with spectral interference. A spectral interference check solution ensures that there is no spectral interference for the analytical lines chosen. These results are listed in **Table 3**.

The calibration was verified using an independent Quality Control Solution (QCS). As required by the U.S. EPA Method 200.7, this solution was prepared from a separate stock solution than the standards. The recovery of all analytes in the QCS were within 5% of the known concentration as required by Method 200.7. These results are listed in **Table 4**.

Before samples, after samples, and between every ten samples an instrument performance check solution, or IPC, must be run to ensure that the instrument is working properly and that all results are accurate. According to Method 200.7, the recovery of the analytes should be within 10% of the known value. The results of the initial IPC solution fall within the acceptable range and are listed in **Table 5**.

EPA 200.7 defines the Linear Dynamic Range (LDR). Samples above the LDR require dilution. A large LDR minimizes this extra labor and is advantageous for measuring a wide variety of environmental samples. The LDR's for each element are listed in **Table 6**.

A lab fortified spike sample was also analyzed and the results are listed in **Table 7**.

A trace drinking water standard, CRM-TMDW, was analyzed without dilution on two consecutive days. The results are listed in **Table 8**.

Table 2: Wavelengths used and detection limits
NOTE: IDLs were determined from single element standards.

Element	Wavelength (nm)	View	IDL (ug/L)	MDL (ug/L)
Al	394.403	axial	0.5	0.5
Ag	328.068	axial	0.3	0.5
As	193.759	axial	4.0	11
Ba	230.424	axial	0.01	0.10
Be	313.042	axial	0.02	0.03
Be	313.042	radial	0.06	0.09
B	249.678	axial	0.2	0.6
B	249.678	radial	0.9	3.1
Ca	315.887	axial	0.005	0.8
Ca	315.887	radial	3.3	4.2
Cd	226.502	axial	0.1	0.2
Ce	418.660	axial	2.0	1.1
Cr	205.552	axial	0.3	0.5
Co	228.616	axial	0.2	0.23
Cu	324.754	axial	0.4	0.4
Fe	259.940	axial	0.1	0.4
Fe	259.940	radial	0.3	1.4
Pb	220.353	axial	2.0	1.0
Li	670.784	radial	3.6	4.3
Mg	383.826	axial	0.005	1.9
Mn	257.610	axial	0.03	0.07
Mo	202.030	axial	0.5	0.7
Ni	231.604	axial	0.3	0.6
Na	589.592	radial	13.0	18.1
P	178.287	axial	5.0	10.9
K	766.490	radial	53.4	90.1
Sb	206.833	axial	3.0	6.3
Se	196.090	axial	4.0	5.8
Si	251.611	axial	0.5	27.2
Sn	189.980	axial	1.0	2.2
Sr	421.552	axial	0.007	0.03
Sr	421.552	radial	0.1	0.2
Ti	337.280	axial	0.1	0.2
Tl	351.924	axial	3.0	4.8
Zn	213.856	axial	0.2	0.5
V	292.402	axial	0.2	0.4

Table 3: Spectral Interference Check

Element	Wavelength (nm)	View	Known Concentration (mg/L)	Measured Concentration (mg/L)	% Recovery
Al	394.403	axial	30	30.8	103
Ag	328.068	axial	3	2.82	94.0
As	193.759	axial	10	9.93	99.3
Ba	230.424	axial	3	2.85	95.0
Be	313.042	axial	1	0.99	98.9
Be	313.042	radial	1	0.96	95.8
B	249.678	axial	5	5.05	101
B	249.678	radial	5	4.96	99.2
Ca	315.887	axial	150	Saturated	NA
Ca	315.887	radial	150	144	96.0
Cd	226.502	axial	3	2.96	98.7
Cr	205.552	axial	3	2.98	99.3
Co	228.616	axial	3	2.88	96.0
Cu	324.754	axial	3	2.91	97.0
Fe	259.940	axial	125	Saturated	NA
Fe	259.940	radial	125	121	96.8
Pb	220.353	axial	10	9.84	98.4
Mg	383.826	axial	75	76.6	102
Mn	257.610	axial	2	1.94	97.0
Mo	202.030	axial	3	2.88	96.0
Ni	231.604	axial	3	2.97	99.0
Na	589.592	radial	25	25.2	101
K	766.490	radial	200	197	98.5
Se	196.090	axial	5	5.10	102
Si	251.611	axial	2.3	2.19	95.2
Ti	337.280	axial	10	9.47	94.7
Tl	351.924	axial	10	9.65	96.5
Zn	213.856	axial	3	3.04	101
V	292.402	axial	3	2.90	96.7

Table 4: QCS Results

Element	Wavelength (nm)	View	Known Concentration (mg/L)	Measured Concentration (mg/L)	% Recovery
Al	394.403	axial	1	1.03	103
Ag	328.068	axial	0.25	0.24	96.8
As	193.759	axial	2	1.95	97.5
Ba	230.424	axial	1	0.97	97.0
Be	313.042	axial	1	1.00	100
Be	313.042	radial	1	1.02	102
B	249.678	axial	1	1.01	101
B	249.678	radial	1	1.03	103
Ca	315.887	axial	1	1.03	103
Ca	315.887	radial	1	1.00	100
Cd	226.502	axial	1	1.01	101
Ce	418.660	axial	1	0.98	98.1
Cr	205.552	axial	1	1.01	101
Co	228.616	axial	1	0.99	99.4
Cu	324.754	axial	1	0.99	99.1
Fe	259.940	axial	1	1.00	100
Fe	259.940	radial	1	0.98	97.5
Pb	220.353	axial	2	2.00	100
Li	670.784	radial	1	1.01	101
Mg	383.826	axial	1	0.96	95.8
Mn	257.610	axial	1	1.02	102
Mo	202.030	axial	1	0.96	96.2
Ni	231.604	axial	1	1.03	103
Na	589.592	radial	1	1.01	101
P	178.287	axial	5	4.83	96.6
K	766.490	radial	5	5.14	103
Sb	206.833	axial	2	2.01	101
Se	196.090	axial	1	1.00	100
Si	251.611	axial	5	4.75	95.0
Sn	189.980	axial	5	4.96	99.2
Sr	421.552	axial	1	1.00	100
Sr	421.552	radial	1	1.00	102
Ti	337.280	axial	1	0.97	96.8
Tl	351.924	axial	5	4.91	98.2
Zn	213.856	axial	1	1.03	103
V	292.402	axial	1	0.96	95.5

Table 5: Initial IPC Results

Element	Wavelength (nm)	View	Known Concentration (mg/L)	Measured Concentration (mg/L)	% Recovery
Al	394.403	axial	2	2.12	106
Ag	328.068	axial	0.25	0.236	94.4
As	193.759	axial	2	1.91	95.5
Ba	230.424	axial	2	1.92	96.0
Be	313.042	axial	2	Saturated	NA
Be	313.042	radial	2	1.99	99.5
B	249.678	axial	2	2.03	102
B	249.678	radial	2	2.04	102
Ca	315.887	axial	2	2.04	102
Ca	315.887	radial	2	2.00	100
Cd	226.502	axial	2	2.00	100
Ce	418.660	axial	2	1.95	97.5
Cr	205.552	axial	2	2.01	101
Co	228.616	axial	2	1.95	97.5
Cu	324.754	axial	2	1.95	97.5
Fe	259.940	axial	2	2.00	100
Fe	259.940	radial	2	1.96	98.0
Pb	220.353	axial	2	1.97	98.5
Li	670.784	radial	2	1.98	99.0
Mg	383.826	axial	2	1.98	99.0
Mn	257.610	axial	2	2.01	101
Mo	202.030	axial	2	1.91	95.5
Ni	231.604	axial	2	2.04	102
Na	589.592	radial	2	1.91	95.5
P	178.287	axial	10	9.59	95.9
K	766.490	radial	10	10.1	101
Sb	206.833	axial	2	2.03	102
Se	196.090	axial	2	1.97	98.5
Si	251.611	axial	10	9.39 (SiO_2)	93.9 (SiO_2)
Sn	189.980	axial	2	1.98	99.0
Sr	421.552	axial	2	Saturated	NA
Sr	421.552	radial	2	1.98	99.0
Ti	337.280	axial	2	1.92	96.0
Tl	351.924	axial	2	2.00	100
Zn	213.856	axial	2	2.02	101
V	292.402	axial	2	1.91	95.5

Table 6: Linear Dynamic Range

Element	Wavelength (nm)	View	LDR (mg/L)
Al	394.403	axial	200
Ag	328.068	axial	10
As	193.759	axial	200
Ba	230.424	axial	20
Be	313.042	axial	2
Be	313.042	radial	10
B	249.678	axial	10
B	249.678	radial	10
Ca	315.887	axial	100
Ca	315.887	radial	100
Cd	226.502	axial	20
Ce	418.660	axial	20
Cr	205.552	axial	50
Co	228.616	axial	20
Cu	324.754	axial	40
Fe	259.940	axial	50
Fe	259.940	radial	100
Pb	220.353	axial	100
Li	670.784	radial	50
Mg	383.826	axial	50
Mn	257.610	axial	10
Mo	202.030	axial	100
Ni	231.604	axial	20
Na	589.592	radial	50
P	178.287	axial	100
K	766.490	radial	100
Sb	206.833	axial	200
Se	196.090	axial	50
Si	251.611	axial	50
Sn	189.980	axial	40
Sr	421.552	axial	2
Sr	421.552	radial	5
Ti	337.280	axial	50
Tl	351.924	axial	50
Zn	213.856	axial	50
V	292.402	axial	40

Table 7: LFS Results

Element	Wavelength (nm)	View	Known Concentration (mg/L)	Measured Concentration (mg/L)	% Recovery
Al	394.403	axial	2	2.04	102
Ag	328.068	axial	0.075	0.068	91.2
As	193.759	axial	0.8	0.75	93.4
Ba	230.424	axial	0.2	0.18	92.0
Be	313.042	axial	0.2	0.19	93.0
Be	313.042	radial	0.2	0.20	98.0
B	249.678	axial	0.3	0.28	94.3
B	249.678	radial	0.3	0.29	97.7
Ca	315.887	axial	1	0.93	92.7
Ca	315.887	radial	1	0.96	95.9
Cd	226.502	axial	0.2	0.19	92.5
Ce	418.660	axial	2	2.03	102
Cr	205.552	axial	0.4	0.38	95.0
Co	228.616	axial	0.2	0.18	90.5
Cu	324.754	axial	0.3	0.29	96.7
Fe	259.940	axial	3	2.94	98.0
Fe	259.940	radial	3	3.05	102
Pb	220.353	axial	1	0.91	91.1
Li	670.784	radial	0.2	0.18	88.5
Mg	383.826	axial	2	1.98	99.0
Mn	257.610	axial	0.2	0.19	93.5
Mo	202.030	axial	0.4	0.40	100
Ni	231.604	axial	0.5	0.49	98.4
Na	589.592	radial	3	2.64	88.0
P	178.287	axial	6	5.56	92.7
K	766.490	radial	10	8.77	87.7
Sb	206.833	axial	0.8	0.80	99.5
Se	196.090	axial	2	1.93	96.5
Si	251.611	axial	2 (SiO_2)	1.89 (SiO_2)	94.5 (SiO_2)
Sn	189.980	axial	0.7	0.69	98.7
Sr	421.552	axial	0.2	0.20	99.0
Sr	421.552	radial	0.2	0.19	92.5
Ti	337.280	axial	0.2	0.21	104
Tl	351.924	axial	2	2.02	101
Zn	213.856	axial	0.2	0.19	96.0
V	292.402	axial	0.3	0.28	93.0

Table 8: CRM-TMDW Results

Element	Wavelength (nm)	View	Known Concentration (ug/L)	Day 1 Measured Concentration (ug/L)	Day 1 % Recovery	Day 2 Measured Concentration (ug/L)	Day 2 % Recovery
Al	394.403	axial	120	91.5	76.3	97.5	81.3
Ag	328.068	axial	2	1.9	95.0	2.2	110.0
As	193.759	axial	80	79.9	100	85.8	107.3
Ba	230.424	axial	50	46.1	92.2	47.3	94.6
Be	313.042	axial	20	20.1	101	21.7	108.5
Be	313.042	radial	20	18.8	94.0	18.8	94.0
Ca	315.887	axial	35000	33600	96.0	36500	104.3
Ca	315.887	radial	35000	36100	103	36600	104.6
Cd	226.502	axial	10	10.4	104	10.2	102.0
Cr	205.552	axial	20	18.3	91.5	22.4	112.0
Co	228.616	axial	25	23.1	92.4	24.8	99.2
Cu	324.754	axial	20	19.2	96.0	20.5	102.5
Fe	259.940	axial	100	94.7	94.7	100	100.0
Fe	259.940	radial	100	83.1	83.1	88.3	88.3
Pb	220.353	axial	40	35.0	87.5	38	95.0
Li	670.784	radial	20	18.8	94.0	20.2	101.0
Mg	383.826	axial	9000	8740	97.1	9040	100.4
Mn	257.610	axial	40	36.8	92.0	38	95.0
Mo	202.030	axial	100	99.2	99.2	104	104.0
Ni	231.604	axial	60	55.5	92.5	55.3	92.2
Na	589.592	radial	6000	5530	92.2	5790	96.5
K	766.490	radial	2500	2410	96.4	2430	97.2
Sb	206.833	axial	10	9.9	99.0	12.8	128.0
Se	196.090	axial	10	11.4	114	9.2	92.0
Sr	421.552	axial	250	243	97.2	246	98.4
Sr	421.552	radial	250	258	103	244	97.6
Tl	351.924	axial	10	7.8	78.0	9.2	92.0
Zn	213.856	axial	70	69.8	100	66.8	95.4
V	292.402	axial	30	29.9	100	29.9	99.7

■ Conclusion

This study demonstrates that the Shimadzu ICPE-9820 is capable of producing results that comply with U.S. EPA Method 200.7. With the addition of the ASC-9800 Auto-sampler and the Standard Addition Kit, the spectrometer is well equipped to handle environmental samples quickly and accurately.

■ Reference

1) https://www.inorganicventures.com/

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