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The use of a dual-view ICP to determine metal concentrations in difficult samples

INDUCTIVELY COUPLED plasma (ICP) has been used as an excitation source for analytical atomic emission spectroscopy for approximately 20 years. During this time, atomic emission spectroscopy (AES) has become the dominant method for trace metals analysis. In response to the continued requirements for better detection limits for some elements, axially viewed ICP was introduced commercially in the last few years. This alternative viewing mode has provided an overall improvement in detection limits, by approximately a factor of 10, over radial ICP. Axial ICP is not without difficulties. It is well known that axial ICP can be more sensitive to matrix effects, such as the Easily Ionized Element (EIE) effect. In addition, high concentrations are more problematic due to the shift of linear dynamic range to lower concentrations exhibited by axial ICP.

The obvious solution to the problem is to design an ICP capable of both radial and axial viewing modes. Such a system would be able to handle virtually any matrix. The purpose of this application note is to demonstrate the utility of a direct reading echelle (DRE) ICP (**Leeman Labs**, Hudson, NH) with optional dual-view capability.

Instrumental

A DRE Axial ICP with optional dual-view capability (**Leeman Labs**) was used. The system combines the high resolution and dispersion of a

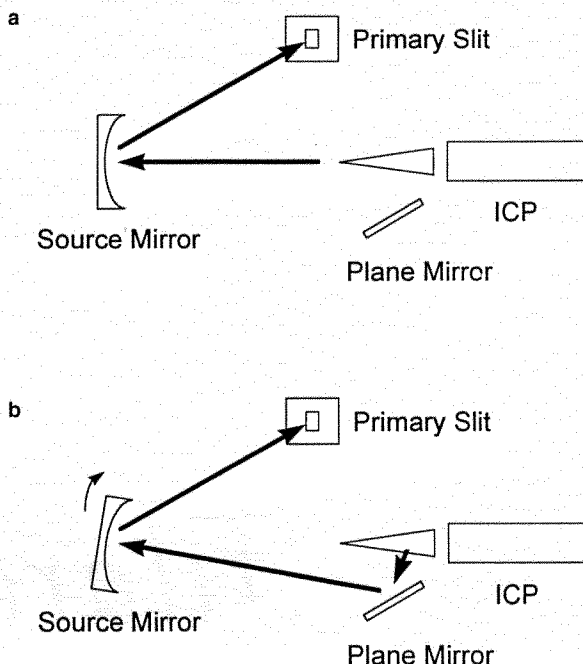


Figure 1 Axial (a) and radial (b) viewing paths. A small movement of the computer-controlled source mirror switches the viewing mode.

photomultiplier tube (PMT)-based echelle optical system and the good detection limit capabilities of axial ICP. In order to allow radial viewing, a plane mirror is positioned close to the side of a slotted torch to direct the light from the plasma onto a computer-controlled focusing mirror. This mirror reflects the light onto the spectrometer's entrance slit. By changing the angle of the focusing mirror, either axial or radial views can be directed to the spectrometer (see *Figure 1*). An advantage of this simple design is both views can be used in a single analytical method. The operator simply selects the desired view using a software switch when setting up the analytical method. Rerunning samples in order to switch views is unnecessary.

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Table 1

Measurement parameters				
Element	View	λ (nm)	Background offset (nm)	Integration time (sec)
Ag	Axial	328.068	-0.026	1
As	Axial	188.977	-0.018	5
Ba	Axial	455.403	0.052	1
Be	Axial	313.042	-0.033	1
Cd	Axial	214.438	-0.025	1
Co	Axial	228.616	-0.024	1
Cr	Axial	267.716	0.033	1
Cu	Axial	324.754	0.040	1
Mn	Axial	257.610	0.030	1
Ni	Axial	231.604	0.025	3
Pb	Axial	220.353	-0.020, 0.020	5
Sb	Axial	206.833	-0.018	5
Se	Axial	196.026	-0.016	5
Tl	Axial	190.801	0.010	5
V	Axial	310.230	0.030	1
Zn	Axial	213.856	-0.027	1
Al	Radial	308.215	0.033	0.5
Ca	Radial	327.933	-0.037	0.5
Fe	Radial	259.940	0.023	0.5
K	Radial	766.490	0.048	0.5
Mg	Radial	285.213	0.033	0.5
Na	Radial	589.592	0.047	0.5

Sample preparation

Soil is considered to be a difficult sample type. The concentrations of the elements of interest range from graphite furnace levels (As and Tl) to percent levels (Ca and Mg). In the past, this type of sample would require analysis on both a radial ICP and a graphite furnace. However, with the use of an ICP with optional dual-view capability, the low-concentration elements can be determined using the axial view, while the high-concentration elements are measured using the radial view. This application note will demonstrate the determination performed on an axial system with dual-view option.

Five certified soil samples were prepared and analyzed: ERA 212 and 228 (**Environmental Resource Associates**, Arvada, CO) and Standard Reference Materials (SRMs) 2709, 2710, and 2710 (NIST, Gaithersburg, MD). In each case, approx. 1 g of soil was prepared and diluted to 100 mL. Each of the soils was prepared by following

Table 2

Instrumental conditions	
Parameter	Setting
Coolant gas	18 L/min
Auxiliary gas	0.5 L/min
Nebulizer gas	50 psi
RF power	1.1 kW
Pump rate	1.6 mL/min

Table 3

Element	ERA 228		Certified value, mg/kg	Advisory range, mg/kg
	Concentration found, mg/kg	RSD, %		
Ag	97.2	0.44	89	130-40.5
As	65.4	1.49	65.4	97.4-32
Ba	168	1.18	161	211-11.3
Be	125	2.17	122	171-78.1
Cd	84.8	0.66	85.4	123-44
Co	107	1.68	94.2	134-56.5
Cr	75.7	0.49	71.6	101-38.7
Cu	173	0.30	173	251-98.6
Mn	343	0.34	298	402-209
Ni	69.8	0.25	68.5	100-37.7
Pb	69.4	1.28	70.4	100-37.3
Sb	39.7	2.34	38.1	68.6-11.4
Se	149	0.71	152	226-79
Tl	88.0	1.66	71.8	117-26.4
V	118	0.25	105	142-73.5
Zn	129	0.63	110	134-59.4
Al	7240	1.08	6070	8668-2730
Ca	4150	0.30	3710	5230-2340
Fe	14,600	0.65	12,500	18,800-6380
K	3870	0.95	3250	4290-2010
Mg	2990	0.92	2490	3590-1490
Na	215	1.67	167	262-71.1

U.S. EPA Method 3050B.¹ This procedure results in a sample from which labile or extractable metal concentrations, not total concentrations, can be measured. PlasmaPure[®] (**Leeman Labs**) calibration standards were prepared from multielement stock solutions in appropriate concentrations. The acid concentration of the standards was carefully matched to the acid concentration of the prepared soil samples.

Results and discussion

The soil samples were analyzed in accordance with U.S. EPA Method 6010B.² Each element was calibrated using three standards plus a blank. In ad-

Table 4

ERA 212				
Element	Concentration found, mg/kg	RSD, %	Certified value, mg/kg	Advisory range, mg/kg
Ag	38.9	1.14	37	56-18
As	15.3	2.79	15	25-5.6
Ba	144	0.98	134	174-93
Be	14.0	0.84	15	21-9.5
Cd	92.8	0.52	109	142-76
Co	193	0.70	211	274-148
Cr	57.2	0.62	41	62-20
Cu	20.5	3.05	20	32-8
Mn	308	0.84	310	403-217
Ni	26.4	0.82	28	48-8
Pb	66.2	0.48	74	111-37
Sb	43.3	1.94	52	160-0
Se	84.6	1.91	91	136-45
Tl	79.1	0.11	99	150-48
V	59.4	0.50	57	74-40
Zn	71.1	0.84	71	80-26
Al	12,390	0.87	11,500	16,500-6530
Ca	7500	1.29	7130	9270-4990
Fe	17,650	1.11	14,500	20,150-10,100
K	3820	1.10	3790	4930-2650
Mg	3830	0.85	3620	4710-2530
Na	527	0.39	400	627-173

Table 5

Montana soil (elevated) NIST 2710				
Element	Concentration found, mg/kg	RSD, %	Median value, mg/kg	Range, mg/kg
Ag	31.9	1.39	28	30-24
As	598	0.98	590	600-490
Ba	318	0.8	360	400-300
Cd	17.3	1.56	20	26-13
Co	8.69	2.98	8.2	12-6.3
Cr	19.5	2.31	19	23-15
Cu	2760	0.93	2700	3400-2400
Mn	8466	0.8	7700	9000-6200
Ni	12.7	0.42	10.1	15-8.8
Pb	6840	0.26	5100	7000-4300
Sb	7.9	7.16	7.9	12-3.4
Se	ND	-	0.002	-
Tl	ND	-	0.63	0.76-0.5
V	44	0.1	43	50-37
Zn	6350	0.28	5900	6900-5200
Al (wt %)	2.0	1.27	1.8	2.6-1.2
Ca (wt %)	0.43	1.43	0.41	0.48-0.38
Fe (wt %)	2.90	0.61	2.7	3.2-2.2
K (wt %)	0.42	0.2	0.45	0.50-0.37
Mg (wt %)	0.55	0.59	0.57	0.60-0.43
Na (wt %)	0.057	1.06	0.054	0.062-0.049

dition, all measurements included background correction using equivalent on-peak and off-peak integration times. Element parameters and analysis con-

Table 6

Montana soil (moderate) NIST 2711				
Element	Concentration found, mg/kg	RSD, %	Median value, mg/kg	Range, mg/kg
Ag	5.4	6.15	4	5.5-2.5
As	87.1	0.90	90	110-88
Ba	176	0.55	200	260-170
Cd	33.1	0.701	40	46-32
Co	8.00	4.19	8.2	12-7
Cr	19.7	1.52	20	25-15
Cu	101	2.37	100	110-91
Mn	491	0.14	490	620-400
Ni	15.1	0.66	16	20-14
Pb	1060	0.70	1100	1500-930
Sb	7.20	1.38	<10	-
Se	ND	8.11	0.009	-
V	44.2	0.82	42	50-34
Zn	295	0.91	310	340-290
Al (wt %)	1.97	0.65	1.8	2.3-1.2
Ca (wt %)	2.18	0.22	2.1	2.5-2.0
Fe (wt %)	2.54	0.77	2.2	2.6-1.7
K (wt %)	0.46	0.2	0.38	0.53-0.26
Mg (wt %)	0.75	1.28	0.81	0.89-0.72
Na (wt %)	0.028	0.67	0.026	0.029-0.020

Table 7

San Joaquin soil (NIST 2709)				
Element	Concentration found, mg/kg	RSD, %	Median value, mg/kg	Range, mg/kg
Ag	7.46	4.14	<20	-
Ba	378	1.22	398	400-392
Cd	0.54	4.79	<1	-
Co	11.5	2.01	12	15-10
Cr	66.0	0.73	79	115-60
Cu	30.0	2.22	32	40-26
Mn	470	0.3	470	600-360
Ni	64.9	1.08	78	90-65
Pb	14.6	2.91	13	18-12
Sb	3.7	7.2	<10	-
Se	ND	-	0.014	-
V	63.9	0.79	62	70-51
Zn	99.1	1.03	100	120-87
Al (wt %)	2.80	0.93	2.6	3.1-2.0
Ca (wt %)	1.58	0.52	1.5	1.7-1.4
Fe (wt %)	3.15	1.15	3.0	3.3-2.5
K (wt %)	0.34	0.55	0.32	0.37-0.26
Mg (wt %)	1.34	1.35	1.4	1.5-1.2
Na (wt %)	0.079	0.63	0.068	0.11-0.063

ditions are shown in *Tables 1* and *2*, respectively. Immediately following calibration, a check standard with concentrations corresponding to the midpoint of each element's calibration range was analyzed. All results were within the required 90-110% recovery. Each soil sample was then analyzed. The results are presented in *Tables 3-7*. All concentration data are in mg/kg, unless noted otherwise.

The DRE ICP accommodated all of the soil samples for analysis. Examination of the data tables indicates the results for all elements lie well within the Performance Acceptance Limits (PAL) for the ERA soils or the range specified for the NIST SRM soils. In addition, the results are in good agreement with the certified values for both soil sets.

The results demonstrate excellent precision, as indicated by the low RSD data in each table, indicating the instrument is operating above the detection limit (DL) and limit of quantitation (LOQ) for the elements determined. This means the analysis can be performed with a high degree of confidence. The detection limits for the method are presented in *Table 8*.

It is important to note that no interelement corrections (IEC) were required in any of these analyses. The versatility of unlimited wavelength selection coupled with the excellent resolution and dispersion of the DRE optical system allowed selection of highly sensitive wavelengths free from spectral overlap. In addition, the high dispersion (the separation of wavelengths at the detector) allows the use of a wide entrance slit without degrading resolution. This permits a large amount of light to reach the detector. Consequently, excellent detection limits are obtained at the maximum resolution of the instrument without having to use extremely long integration times. The amount of time required to determine all 22 elements using the integration times in *Table 2* with background correction, including sample uptake and rinse, was just over 5 min.

Conclusion

The DRE ICP equipped with optional dual-view capability is an appropriate choice to increase the versatility of the ICP. The additional capability permits the analysis of samples that would

Table 8

Element	Detection limits in original sample
	Detection limit mg/kg
Ag	0.008
As	0.502
Ba	0.016
Cd	0.026
Co	0.106
Cr	0.053
Cu	0.092
Mn	0.009
Ni	0.211
Pb	0.221
Sb	0.343
Se	0.529
Ti	0.634
V	0.057
Zn	0.053
Al	0.251
Ca	0.026
Fe	0.065
K	0.660
Mg	0.004
Na	0.290

otherwise have to be analyzed on multiple instruments that may require additional digestion procedures, decreasing overall productivity and increasing waste disposal costs.

Contrary to published reports,³ the addition of dual-view capability need not introduce significant optical complexity when designed carefully, nor does it degrade the enhanced sensitivity of the axially viewed ICP.

References

1. Test methods for evaluating solid waste, physical/chemical methods, SW 846, proposed update III, Method 3050B, Washington, DC: U.S. EPA, 1992.
2. Test methods for evaluating solid waste, physical/chemical methods, SW 846, proposed update III, Method 6010B, Washington, DC: U.S. EPA, 1992.
3. Thomas GP. *Am Environ Lab* 1997; 9(3):28-30.