



The determination of major and minor elements in air filters and urine for hazard assessment, using a new CCD DUAL-VIEWED ICP OPTICAL EMISSION SPECTROMETER

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Abstract

This article describes the application of a new type of CCD-based, dual-viewed ICP optical emission spectrometer for the analyses of industrial hygiene types of samples. Several trace elements in air filter media are determined by ICP-OES. Urinary electrolytes and trace elements are determined in a single dilution automatically in both the axial and radial plasma viewing orientations. Results of the analyses of certified reference materials are presented. Instrumental parameters and conditions are presented and discussed.

Introduction

Many metal-based industries require the regular monitoring of their facilities to insure a safe and healthy working environment. OSHA has set exposure limits for many hazardous elements in workplace air (1). Often this task takes the form of air monitoring, whereby a known quantity of a building's internal air is drawn through a membrane filter. The filter traps the metal-containing dust particles. The filter membrane and its contents are then digested or leached into a known volume of solution. Inductively coupled plasma optical emission spectrometry (ICP-OES) provides accurate and rapid quantitative elemental analyses of the solution, so that the amount of

airborne metal (mg/m^3) in the facility's air can be determined (2-3).

Additionally, it may be desirable to periodically screen employees for evidence of exposure to toxicologically significant levels of hazardous elements. Measuring urinary levels of these elements by ICP-OES is a rapid and convenient means to assessing workers' exposures. Historically, atomic absorption spectroscopy (flame and electrothermal atomization) has been the technique of choice for most analysts. High concentrations of the electrolytes, sodium, potassium, calcium, and magnesium have been measured in urine for many years by flame AAS (4-5), and more recently ICP-OES has been used to provide multielement determinations of these elements (6-7). Very low concentrations of many trace elements in urine have been reported in the literature using electrothermal AAS (8-10), but very few trace elements provide sufficient signal for traditional photomultiplier tube-based ICP spectrometers using radial plasma viewing without a preconcentration step (11-12).

Since its introduction 30 years ago, ICP-OES has found wide application in many fields by providing efficient multielemental spectrochemical analysis. However, when compared with electrothermal atomic absorption, traditional or

radially viewed ICPs have had the disadvantage of lower sensitivity. This is especially important in the application of ICP-OES to the determination of trace elements in urine, because many of the elements are toxicologically important at very low concentrations (mg/L). More recently, axially-viewed ICP-OES has extended the measurable concentration range into the sub-ppb area for many elements (13-14). Axial observation samples a larger volume of the plasma emission, potentially yielding improved detection limits by up to a factor of 10.

Solid-state charge-coupled device (CCD) detectors have been applied to the measurement of ICP spectra recently with great advantages (15-16). The array detectors give the analyst the most flexibility in choice of analytical wavelengths and background correction points. These CCD detectors simultaneously measure the analytical line and the spectral background, thereby reducing background flicker noise and improving the measurement's signal-to-noise ratio.

A new high-speed, Charge-Coupled Detector-based ICP-OES instrument with the ability to set the plasma viewing orientation (radial or axial) on an element-by-element basis was used for these analyses. The

determination of trace elements in urine using the newer axially viewed plasma has not been widely described in the literature.

Experimental

Instrumentation and Operating Conditions

A PerkinElmer Optima 2000™ DV optical emission spectrometer was used for all determinations. The spectrometer is a high-energy (f/6) echelle-based monochromator. The spectrometer has full wavelength coverage from 165 to 800 nm with a resolution of approximately 0.009 nm at 200 nm. The entire optical system is enclosed and can be purged with nitrogen or argon for operation in the low UV.

The two-dimensional ICP spectral image is focussed on the linear CCD array detector for simultaneous measurement of spectral peaks and neighboring spectral background areas. Minimum and maximum integration times are user-selectable with the actual time selected by the instrument based on the emission signal intensity (Auto-integration). Intense emission peaks are integrated with shorter integration times, and weak signals are integrated with the maximum time, thus optimizing precision of analysis. The CCD is Peltier-cooled to -8°C for improved signal-to-noise ratio measurements.

The plasma RF generator is of a total solid-state design, operating in the free-running mode nominally at 40 Mz. The power is user-selectable in 1-watt increments from 750 to 1500 watts. The instrument controls all plasma gas flows with mass-flow control of the nebulizer argon.

The ICP torch is physically mounted in an axial orientation in the instrument's shielded torch box, but can be viewed either axially or radially. The view mode is user-selectable on an element-by-element basis. The X-Y (axial) and

Y (radial) position is automatically optimized by the instrument. A shear gas flow provides elimination of the cool ICP tail to allow direct observation of the plasma's normal analytical zone, thus minimizing chemical matrix effects when the axial-view mode is employed.

A cyclonic spray chamber was used to provide both high sample transfer into the ICP and very fast sample rinse in/out times. A Babington-type low flow Gem-Cone™ nebulizer (PerkinElmer, Norwalk, CT) was used for this work. It was chosen because of its high tolerance for particulates, as may be found in digested air filter samples, and because of the excellent ability to aspirate samples with high total dissolved solids (TDS) as in the case of the urines. Table 1 lists the instrumental conditions used.

All instrumental parameters are controlled from a computer, using Windows NT® version 4.0 operating system and PerkinElmer ICP WinLab32™ application software. Analytical data and methods are handled in compliance with GLP and GALP recommendations.

Sampling Preparation

Two air filter samples were obtained from the NIST. Standard Reference Material (SRM) number 3087a (Metals on Filter Media) is a cellulose ester-type membrane that has been spiked by NIST with a mixed standard of several elements. Also supplied are several blank filters used for digestion blanks. Each filter is 37 mm diameter with a pore size of 0.8 mm. The second reference sample is SRM number 2677a (Beryllium and Arsenic on Filter Media). For this work, Level II and a blank were used and analyzed for arsenic and beryllium, only.

Individual air filters were digested in cleaned glass beakers with 2 mL conc. nitric acid (GFS Chemicals, Columbus, OH) and gentle warming until dissolved.

They were brought to a volume of 50 mL in high-density polyethylene bottles. Yttrium was added at a concentration of 1 mg/L for use as an internal standard.

A freeze-dried urine standard reference material was prepared (NIST 2670 Toxic Metals in Freeze-Dried Urine). This SRM consists of two samples, a low level and an elevated level. The SRM was reconstituted by adding 20 mL of ASTM Type 1 water directly to each sample vial. Once fully reconstituted, the SRM samples were transferred to plastic bottles, diluted in half with laboratory-pure water, and acidified to 2% concentrated nitric acid. Scandium and yttrium internal standards were added to each sample with a resulting concentration of 1 mg/L. Reagent blanks were prepared in a similar manner.

In addition to the SRMs, several fresh urine samples were collected from volunteers. These were a male smoker, a male non-smoker, and a female vegetarian who had a recent seafood meal. Urine samples were

Table 1. Instrumental Conditions and Operating Parameters, Optima 2000 DV

RF Power	1450 watts
Nebulizer Flow	0.65 L/min
Auxilliary Flow	0.5 L/min
Plasma Flow	15 L/min
Sample Pump Flow	1.5 mL/min
Plasma Viewing	Dual View
Processing Mode	Area
Auto Integration (min-max)	1-5 s
Read Delay	40 s
Rinse	-
Replicates	3
Background Correction	Manual, one or two points
Nebulizer GemCone™	Low-flow
Nebulizer Chamber	Cyclonic
Injector	Alumina, 2 mm

collected in low-density polyethylene bottles. Samples were diluted in half with laboratory-pure water and acidified to 2% with concentrated nitric acid. Scandium and yttrium internal standards were added to each sample at this point, to a concentration of 1 mg/L. Reagent blanks were prepared in a similar manner.

Standards and Reagents

Instrumental calibration standards were prepared by serial dilution P-E Pure 1000 ppm stocks and pre-mixed standards. Deionized type I water was used for all dilutions. Nitric acid was Optima grade from Fisher Sci. Co. Blank solutions were prepared from the same materials. Scandium and yttrium were added to all standards and blanks for use as internal standard elements.

Sample Analysis

Prior to any analytical measurements being made, the optimal axial ICP observation position was found. For this procedure, a solution containing 1 mg/L of scandium was aspirated. The instrument automatically optimizes signal-to-background ratio by the two-dimensional movements of a stepper motor controlled flat transfer mirror. After calibration, the samples were aspirated without any problems noted. All spectra were stored for the possible post-processing of the data.

The analytical wavelengths and off-line background correction intervals are given in Tables 2 and 3 for the urine and air filter methods developed. The wavelengths were chosen to give the best detection limits with the least spectral interference. In some cases, less sensitive wavelengths were chosen to shift the calibration to a higher linear range, as in the cases of the electrolyte elements in urine. Radial viewing will also change the working range of the emission wavelength. Off-line background correction measurements were made for all analytical wavelengths.

Table 2. Wavelengths, background correction points and plasma view for Urine Samples

Element	Wavelength (nm)	BGC (low)	BGC (high)	View	IEC
Aluminum	396.153	-0.046	0.058	Axial	
Arsenic	193.696	-0.071	0.049	Axial	Ca, Mg
Beryllium	313.107		0.067	Axial	
Cadmium	228.802	-0.063	0.025	Axial	
Calcium	315.887	-0.065	0.065	Radial	
Chromium	267.716	-0.055	0.033	Axial	
Copper	327.393	-0.117	0.070	Axial	
Gold	267.595	-0.044		Axial	
Iron	238.204	-0.050	0.050	Axial	
Lead	220.353	-0.032		Axial	
Magnesium	279.077	-0.035	0.033	Radial	
Manganese	257.61	-0.054	0.054	Axial	
Nickel	231.604	-0.031		Axial	
Platinum	265.945	-0.012		Axial	Ca, Mg
Potassium	404.721	-0.043		Radial	
Scandium (IS)	361.383	-0.074		Radial	
Selenium	196.026	-0.012		Axial	Ca, Mg
Sodium	330.237	-0.057		Radial	
Vanadium	292.464	-0.041		Axial	
Yttrium (IS)	371.029	-0.078	0.078	Axial	

Table 3. Wavelengths, background correction points and view for Air Filter Samples

Element	Wavelength (nm)	BGC (low)	BGC (high)	View
Arsenic	188.979		0.039	Axial
Barium	233.527	-0.049		Axial
Beryllium	313.107		0.047	Axial
Cadmium	226.502		0.041	Axial
Chromium	267.716	-0.048		Axial
Cobalt	228.616	-0.055		Axial
Copper	324.752		0.067	Axial
Iron	238.204		0.034	Axial
Lead	220.353	-0.021	0.019	Axial
Magnesium	285.213	-0.043		Axial
Manganese	257.61	-0.054	0.054	Axial
Nickel	231.604	-0.058		Axial
Selenium	196.026	-0.021	0.024	Axial
Vanadium	292.464		0.025	Axial
Yttrium (IS)	371.029	-0.068	0.068	Axial
Zinc	213.856	-0.026		Axial

The background correction points were selected by overlaying spectra of standards, blanks and several samples and visually choosing one or two points to best compensate for any background around the peak of interest. At least one background correction point was used to take advantage of the signal/noise enhancement of the simultaneity of the background and the line measurement (16).

Results and Discussion

The method developed for urine was tested with a standard reference material and spikes of normal urine collected from volunteers. Table 4 shows the results for the reference material compared with the certified values. The standard deviation of three replicate measurements is shown to indicate the confidence interval that might be calculated for the measured values.

In all cases, the confidence intervals of the certified material and the measured values overlap.

Table 4. Normal and Elevated NIST 2670 Urine Reference Material (mg/L)

Element	2670 Normal Level			2670 Elevated Level		
	Mean Meas.	SD	Cert. Value	Mean Meas.	SD	Cert. Value
Aluminum	0.195	0.0029	(0.180)	0.156	0.0010	(0.18)
Arsenic	0.064	0.0047	0.06	0.540	0.0023	0.48 ± 0.1
Beryllium	0.002	0.0001	(<0.0005)	0.032	0.0002	(0.033)
Cadmium	0.001	0.0001	(0.0004)	0.087	0.0007	0.088 ± 0.003
Calcium	112	0.5	105 ± 5	110	0.2	10 ± 5
Chromium	0.008	0.0001	(0.013)	0.080	0.0003	0.085 ± 0.006
Copper	0.116	0.0013	0.130 ± 0.020	0.391	0.0088	0.371 ± 0.03
Gold	< 0.005	0.0015	(<0.0001)	0.203	0.0064	(0.24)
Iron	0.189	0.0307	-	0.100	0.0022	-
Lead	0.011	0.0024	(0.010)	0.106	0.0009	0.109 ± 0.004
Magnesium	64.2	0.0028	63 ± 3	60.6	0.2	63 ± 3
Manganese	0.026	0.0001	(0.03)	0.337	0.0038	(0.330)
Nickel	0.083	0.0005	(0.07)	0.301	0.0031	(0.30)
Platinum	< 0.004	0.0009	(<0.0001)	0.124	0.0001	(0.12)
Potassium	1475	23	(1500)	1484	5	(1500)
Selenium	< 0.011	0.0036	0.030 ± 0.008	0.509	0.0048	0.46 ± 0.03
Sodium	2469	74	2620 ± 140	2476	44	2620 ± 140
Vanadium	0.007	0.0004	-	0.115	0.0017	(0.12)

Table 5 shows measurements from urines collected from volunteers. The urine was pooled over the course of several hours. The urines were similar to each other and to the NIST low-level urine with the exception of arsenic in the urine collected from a person who had recently dined on two meals of fish.

Table 6 shows spike recoveries from a volunteer urine, spiked with a low concentration of multiple elements. The recoveries of the spiked values are excellent and demonstrate that the method is operating without interference from matrix components.

Table 7 compares the certified values and results for the filter analyses. Arsenic was measured at two different values in the two NIST materials, showing excellent performance of the instrument over a wide concentration range. The total filter value is accompanied by the standard deviation to allow comparison with the certified value. Values were in close agreement except for Zn which, although outside the expected confidence interval, resulted in a recovery of 93% of the certified value. Elements present at high concentrations may cause a spectral interference on elements present at low concentration and of interest as the analyte. Interfering element correction (IEC) factors can be generated and applied to these analytes to correct for spectral interferences. IECs were used to correct for Mg and Ca interferences on As, Pt, and Se in the urine samples.

Table 5. Measurement of Collected Volunteer Urines

Element	Urine, fish diet		Urine, smoker		Urine, nonsmoker	
	Mean Meas.	SD	Mean Meas.	SD	Mean Meas.	SD
Aluminum	0.059	0.0003	0.077	0.0013	0.056	0.0009
Arsenic	0.104	0.0015	< 0.010	0.0034	< 0.010	0.0035
Beryllium	0.001	0.0000	0.002	0.0000	< 0.0005	0.0001
Cadmium	0.001	0.0001	0.005	0.0000	< 0.0005	0.0001
Calcium	87.6	1.7	146	1.0	22.3	0.02
Chromium	< 0.002	0.0005	0.010	0.0007	0.004	0.0012
Copper	< 0.001	0.0004	< 0.001	0.0002	0.045	0.0009
Gold	< 0.004	0.0012	< 0.004	0.0011	< 0.005	0.0016
Iron	0.005	0.0001	0.024	0.0001	0.016	0.0005
Lead	0.009	0.0011	0.032	0.0005	0.016	0.0020
Magnesium	82.4	3.0	155	0.7	31.1	0.1
Manganese	< 0.001	0.0001	0.001	0.0001	0.001	0.0002
Nickel	0.018	0.0001	0.033	0.0006	0.020	0.0005
Platinum	< 0.007	0.0022	0.013	0.0025	< 0.007	0.0020
Potassium	684	3.9	4780	80.5	1207	8
Selenium	0.086	0.0028	0.147	0.0020	0.060	0.0016
Sodium	2230	29	3720	98.2	2010	20
Vanadium	0.001	0.0001	0.001	0.0003	0.001	0.0002

Table 6. Spiked Urine Recoveries (mg/L)

Element	Spike Conc.	Spiked Urine		
		Mean Meas.	SD	% Recov.
Aluminum	0.25	0.340	0.0031	113.6
Arsenic	0.25	0.259	0.0060	101.6
Beryllium	0.25	0.254	0.0008	101.7
Cadmium	0.25	0.257	0.0020	102.6
Calcium		22.5	0.1	
Chromium	0.25	0.257	0.0025	102.1
Copper	0.25	0.278	0.0024	93.2
Gold	0.05	0.050	0.0010	94.0
Iron	0.25	0.258	0.0060	96.8
Lead	0.25	0.260	0.0057	97.6
Magnesium		28.5	0.1	
Manganese	0.25	0.258	0.0083	103.2
Nickel	0.25	0.258	0.0010	95.2
Platinum	0.05	0.054	0.0003	104.0
Potassium		1230	23	
Selenium	0.25	0.286	0.0108	90.4
Sodium		2046	12	
Vanadium	0.25	0.261	0.0020	104.2

Conclusion

The excellent selectivity, sensitivity, and flexibility of the CCD-based ICP spectrometer with axial and radial ICP view can be used to great advantage for the multielemental analysis of complex samples with wide variations in analyte concentration. If traditional atomic absorption methods had been used for this analysis, the analysis time would have increased by a factor of approximately 10 using a single-element system and measuring most of the elements with flame atomic absorption and only using graphite furnace for lead, cadmium, and chromium. Using ICP-OES, the full suite of analytes can be measured in one run and takes approximately five minutes for each urine sample and three minutes for an air filter sample.

Table 7. Results for NIST Air Filter Analyses.

Element	Filter Digest (mg/L)	SD (mg/L)	Blank Filter Digest (mg/L)	SD (mg/L)	Total Filter (µg/Filter) (SD)	Certified (µg/Filter)
Arsenic	0.9648	0.0157	< 0.005	0.0014	48.24 (0.78)	50.48 ± 1.16
Arsenic*	0.0536	0.0025	< 0.005	0.0014	2.68 (0.13)	2.69 ± 0.065
Barium	0.5126	0.0016	< 0.0003	0.0001	25.63 (0.08)	25.24 ± 0.58
Beryllium*	0.0120	0.0001	< 0.0001	0.0000	0.60 (0.05)	0.643 ± 0.015
Cadmium	0.2883	0.0040	< 0.0003	0.0000	14.42 (0.02)	15.14 ± 0.35
Chromium	0.2056	0.0018	< 0.0005	0.0001	10.28 (0.09)	10.10 ± 0.23
Cobalt	<0.001	0.0002	< 0.0005	0.0001	< 0.025	–
Copper	<0.001	0.0002	< 0.001	0.0003	< 0.050	–
Iron	0.5125	0.0088	< 0.001	0.0003	25.63 (0.44)	25.24 ± 0.58
Lead	0.7897	0.0097	< 0.002	0.0006	39.49 (0.49)	40.38 ± .92
Magnesium	0.4931	0.0008	0.0052	0.0002	24.66 (0.04)	25.24 ± 0.58
Manganese	0.1974	0.0009	0.0002	0.0000	9.87 (0.05)	10.10 ± 0.23
Nickel	0.4826	0.0052	0.0006	0.0001	24.13 (0.26)	25.24 ± 0.58
Vanadium	0.9593	0.0062	0.0011	0.0001	47.97 (0.31)	50.48 ± 1.16
Zinc	1.8733	0.0127	0.0041	0.0002	93.67 (0.63)	100.94 ± 2.31

* From NIST 2677a.

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