Inductively-Coupled Plasma/Optical Emission Spectroscopy ICP-OES

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 . 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 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 Insulating materials because many of the elements are toxicologically important at very low concentrations (mg/kg). Axially-viewed ICP-OES has extended the measurable concentration range into the sub-ppb area for many elements. 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. 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 is used for these analyses.

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 by flame AAS, and more recently ICP-OES has been used to provide multi-element determinations of these elements. Very low concentrations of many trace elements have been reported in the literature using electrothermal AAS, but very few trace elements provide sufficient signal for traditional photomultiplier tube-based ICP spectrometers using radial plasma viewing without a preconcentration step. Since its introduction 30 years ago, ICP-OES has found wide application in many fields by providing efficient multi-elemental spectrochemical analysis. However, when compared with electrothermal atomic absorption, traditional or determination of trace elements 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 is 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 neighbouring 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 is 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 (Perkin Elmer) is 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).

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 recommendations.

Sampling Preparation

Standard Reference Material (SRM) Metals on Filter Media is a cellulose ester-type membrane that has been spiked 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 Beryllium and Arsenic on Filter Media. For this work, Level II and a blank are used and analyzed for Arsenic and Beryllium, only.

Individual samples are digested in cleaned glass beakers with 2 mL conc. Nitric acid and gentle warming until dissolved. They are 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 standard reference material is prepared. 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 are transferred to plastic bottles, diluted in half with laboratory-pure water, and acidified to 2% concentrated Nitric acid. Scandium and yttrium internal standards are added to each sample with a resulting concentration of 1 mg/L. Reagent blanks are prepared in a similar manner.

Table 1.

RF Power	1450 watts
Nebulizer Flow	0.65 L/min
Auxiliary Flow	0.05 L/min
Plasma Flow	15 L/min
Sample Pump Flow	1.5 mL/min
Plasma Viewing	Dual View P
Processing Mode	Area
Auto Integration	1-5s Read
Delay	40s
Rinse	-
Replicates	3
Background Correction	Manual
Nebulizer	Low-flow
Nebulizer Chamber	Cyclonic
Injector	Alumina, 2 mm

Standards and Reagents

Instrumental calibration standards are prepared by serial dilution P-E Pure 1000 ppm stocks and pre-mixed standards. Deionized type I water is used for all dilutions. Nitric acid is Optima grade. Blank solutions are prepared from the same materials. Scandium and yttrium are 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 is found. For this procedure, a solution containing 1 mg/L of scandium is 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 are aspirated without any problems noted. All spectra is 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. The wavelengths are chosen to give the best Detection limits with the least spectral interference. In some cases, less-sensitive wavelengths are chosen to shift the calibration to a higher linear range. Radial viewing will also change the working range of the emission wavelength. Off-line background correction measurements are made for all Analytical wavelengths.

Table 2.

Element	Wavelength	BGC (low)	BGC (high)	View	IEC
Aluminium	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	

The background correction points are 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 is used to take advantage of the signal/noise enhancement of the simultaneity of the background and the line measurement.

Results and Discussion

The method developed is tested with a standard reference material and spikes.

Table 3 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. It also shows spike recoveries 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.

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 multi-elemental 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 sample.

Table 3.

Spiked Elemental Recoveries (mg/L)

Element	**Spike Conc.**	**Mean Meas.**	**Standard Deviation**	**% Recovery**
Aluminium	0.25 ppm.	0.315	0.0047	112.6
Arsenic	0.25 ppm.	0.248	0.003	99.2
Beryllium	0.25 ppm.	0.255	0.002	102
Cadmium	0.25 ppm.	0.261	0.004	104.4
Calcium	0.25 ppm.	0.249	0.001	99.6
Chromium	0.25 ppm.	0.239	0.009	95.6
Copper	0.25 ppm.	0.235	0.011	94
Gold	0.25 ppm.	0.251	0.0021	100.4
Iron	0.25 ppm.	0.247	0.004	98.8
Lead	0.25 ppm.	0.245	0.0052	98
Magnesium	0.25 ppm.	0.300	0.008	120
Manganese	0.25 ppm.	0.255	0.0034	102
Nickel	0.25 ppm.	0.247	0.0031	98.8
Platinum	0.25 ppm.	0.252	0.0021	100.8
Potassium	0.25 ppm.	0.270	0.0066	108
Selenium	0.25 ppm.	0.248	0.0023	99.2
Sodium	0.25 ppm.	0.257	0.0024	102.8
Vanadium	0.25 ppm.	0.249	0.0011	99.6
Zinc	0.25 ppm.	0.265	0.0056	106

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