APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Analysis of Impurities in Lead with the Avio 500 ICP-OES Following London Metal Exchange Guidelines

Introduction

Although lead (Pb) is highly toxic to living organisms and has been phased out of a wide variety of products, it is still commonly used in a number of applications, most notably lead-acid batteries, alloys, radiation shielding, flashing in the construction industry, ammunition, and as lining in industrial pipes and baths carrying corrosive substances. With this assortment of uses, the required grade/purity of lead varies; as a result, lead is produced in various purity levels.

The London Metal Exchange issues specifications for a number of different metals in several grades. This work focuses on the analysis of lead of different purities with PerkinElmer's Avio® 500 ICP Optical Emission Spectrometer (ICP-OES), using "Special Contract Rules for Standard Lead[1]" as a guideline for the analytes and concentrations.

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Experimental

Samples

All analyses were performed in 1% solutions of Pb to simulate digests diluted 100x with 5% nitric acid (v/v). To check for accuracy, elemental spikes were added to the 1% Pb solution at the levels set in the "Special Contract Rules for Standard Lead". Calibration standards were prepared in 5% HNO_3 at 50, 100, and 200 ppb in 1% Pb solutions. The "Method of Additions – Sample Intercept" was used as the calibration scheme to overcome matrix effects in the plasma.

Instrumentation

All analyses were performed on the Avio 500 ICP-OES using the parameters in Table 1 and the analytes and wavelengths in Table 2. The standard sample introduction configuration and parameters were used for all analyses. The torch position was set to -4. Combining the simultaneous analysis of the Avio 500 with the low argon consumption (9 L/min total) provides significant savings, when considering the cost of argon.

Table 1. Avio 500 ICP-OES Instrumental Parameters and Conditions.

Parameter	Value
Nebulizer	MEINHARD® K-1
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Injector	2.0 mm ceramic
Plasma Gas Flow	8 L/min
Aux Gas Flow	0.2 L/min
Nebulizer Gas Flow	0.60 L/min
Torch Position	-4
Sample Uptake Rate	1.0 mL/min
Sample Uptake Tubing	Black/Black (0.76 mm id)
Internal Standard Tubing	Green/Orange (0.38 mm id)
Drain Tubing	Red/Red (1.14 mm id)
Replicates	3
Plasma View	Axial

Results and Discussion

The London Metal Exchange lists several different specifications for Pb; this work focused on 99.97% and 99.985% Pb specifications for BS EN 12659:1999 (Lead and Lead Alloys) and GB/T 469-2005 (Lead Ingots), as summarized in Table 3.

To assess the ability to perform accurate measurements at these levels, the analytes were spiked into 1% Pb solutions at the concentrations in Table 4, accounting for a 100x dilution for sample preparation (i.e. pure lead diluted 100x prior to analysis). The plot in Figure 1 shows that all elements at the four different specifications shown in Table 3 recover within 10% of their true values, demonstrating the accuracy of the methodology. Because of spectral interferences on Sn and Zn, a Multicomponent Spectral Fitting (MSF) model[2] was applied to these elements, which removed the effects of the interferences, allowing accurate results at both purity levels.

Table 2. Elements and Wavelengths.

Element	Wavelength (nm)
Ag	243.778
As	193.696
Bi	223.061
Cd	214.440
Cu	327.393
Fe	259.939
Ni	221.648
Sb	231.146
Sn	189.927
Zn	206.200
Sc (int std)	361.383

Table 3. Specifications for Pb Purities Used in this Work.

	BS EN 12659:1999 (Lead and Lead Alloys) 99.97%	99.985%	GB/T 469-2005 (Lead Ingots) 99.97%	99.985%
Element	Concentration (wt %)	Concentration (wt %)	Concentration (wt %)	Concentration (wt %)
Ag	0.005	0.0025	0.005	0.0025
As	0.001	0.0005	0.001	0.0005
Bi	0.03	0.015	0.03	0.015
Cd	0.001	0.0002	0.001	0.0002
Cu	0.003	0.001	0.003	0.001
Fe	---	---	0.002	0.001
Ni	0.001	0.0005	0.001	0.0005
Sb	0.001	0.0005	0.001	0.0008
Sn	0.001	0.0005	0.001	0.0005
Zn	0.0005	0.0002	0.0005	0.0004

Table 4. Analyte Spike Levels in 1% Lead.

Element	Spike Levels (mg/L)
Ag	0.25, 0.5
As	0.05, 0.1
Bi	1.5, 3
Cd	0.02, 0.1
Cu	0.1, 0.3
Fe	0.1, 0.2
Ni	0.05, 0.1
Sb	0.05, 0.08, 0.1
Sn	0.05, 0.1
Zn	0.02, 0.04, 0.05

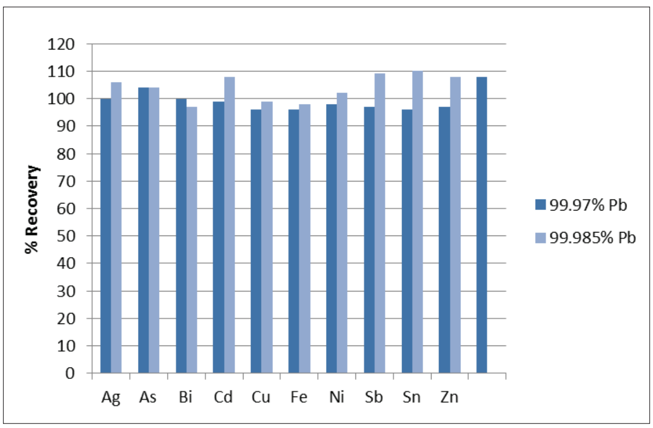

Figure 1. % Recoveries of analytes in 1% Pb, spiked at the 99.97% and 99.985% limits.

To determine the ability to measure even lower concentrations in 1% Pb, elements were spiked into 1% Pb at 20 µg/L, the equivalent of 0.0002 wt %. This concentration is at or below the specifications for 99.990% and 99.994% Pb, as shown in Table 5[1]. The recoveries appear in Figure 2 and demonstrate the ability to accurately measure these lower concentrations with the current methodology.

Table 5. Specifications for 99.990 and 99.994% Lead (units in wt %)

Element	BS EN Lead and Lead Alloys: 99.990%	GB/T Lead Ingots: 99.994%
Ag	0.0015	0.0008
As	0.0005	0.0008
Bi	0.0100	0.004
Cd	0.0002	---
Cu	0.0005	0.001
Fe	---	0.0005
Ni	0.0002	---
Sb	0.0005	0.0008
Sn	0.0005	0.0005
Zn	0.0002	0.0004

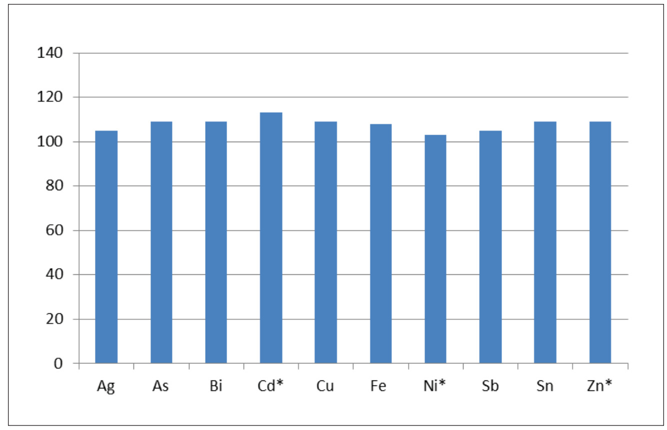

Figure 2. % Recoveries of analytes in 1% Pb, spiked at 0.020 mg/L, representing 0.0002 wt % (* = elements specified at 0.0002 wt % in 99.985% Pb).

With the accuracy established, the stability of the methodology was assessed by monitoring the internal standard signal over a 6-hour analysis of 1% Pb. The results are plotted in Figure 3 and show a variation of less than ± 3% over 6 hours when normalized to the first reading, demonstrating the stability of the methodology.

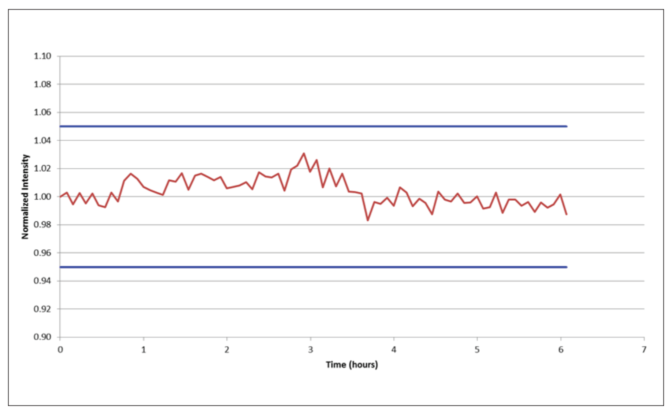

Figure 3. Internal standard (Sc) stability over a 6-hour analysis of 1% Pb. All data is normalized to the first reading.

Conclusions

This work demonstrates the ability of the Avio 500 ICP-OES to analyze solutions of 1% lead for elements at the levels specified by the London Metal Exchange for purities ranging 99.97% up to 99.994%. Although the high-matrix concentration results in spectral interferences for a few of the elements, these can be overcome through the use of MSF, allowing all of the specified elements to be measured at their required concentrations. The Avio 500 is easily able to measure traces in lead to meet the London Metal Exchange requirements.

References

1. "Special Contract Rules for Standard Lead", The London Metal Exchange.

2. "Multicomponent Spectral Fitting", Technical Note, PerkinElmer, 2017.

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	N0777043 (flared) 09908587 (non-flared)
Drain Tubing, Red/Red (1.14 mm id), PVC	09908585
Internal Standard Tubing, Orange/Green (0.38 mm id), PVC	N0773111 (flared)
Antimony Standard, 1000 mg/L	N9300207 (125 mL) N9300101 (500mL)
Arsenic Standard, 1000 mg/L	N9300180 (125 mL) N9300102 (500 mL)
Bismuth Standard, 1000 mg/L	N9303761 (125 mL) N9300105 (500 mL)
Cadmium Standard, 1000 mg/L	N9300176 (125 mL) N9300107 (500 mL)
Copper Standard, 1000 mg/L	N9300183 (125 mL) N9300114 (500 mL)

Component	Part Number
Iron Standard, 1000 mg/L	N9303771 (125 mL) N9300126 (500 mL)
Nickel Standard, 1000 mg/L	N9300177 (125 mL) N9300136 (500 mL)
Scandium Standard, 1000 mg/L	N9303798 (125 mL) N9300148 (500mL)
Silver Standard, 1000 mg/L	N9300171 (125 mL) N9300151 (500 mL)
Tin Standard, 1000 mg/L	N9303801 (125 mL) N9300161 (500mL)
Zinc Standard, 1000 mg/L	N9300178 (125 mL) N9300168 (500 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)

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