APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Analysis of Aluminum Alloys with the Avio 200 ICP-OES Following London Metal Exchange Guidelines

Introduction

Because of its unique characteristics, aluminum (Al) is used in a wide variety of commercial and industrial applications. However, the utility of Al can be enhanced by combining it with other metals to create aluminum-based alloys, where the non-aluminum additives can make up to 15% of the total alloy, by weight. The primary elements added to Al are silicon (Si), iron (Fe), copper (Cu), and zinc (Zn), to improve the alloy's strength compared to pure Al and also enhance the physical characteristics, such as better conductivity and welding capabilities.[1,2] Other elements can also be added in various quantities to further vary the alloy's characteristics.

Because of its popularity and multiple compositions, the London Metal Exchange (LME) lists four different specifications for Al alloy compositions which are primarily used in Europe, Asia, and North America[3,4], shown in Table 1. In these specifications, Si, Cu, Zn, and Fe are considered major additions, as they are mostly greater than 1% composition by weight. Therefore, these four elements must be determined with greater accuracy (± 2%) than the others.

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Most commercial applications of aluminum are aluminum alloys due to their enhanced characteristics compared to pure aluminum. PerkinElmer's Avio® 200 ICP-OES is an ideal choice for laboratories performing this application. The Avio 200 ICP-OES uses a CCD detector, providing simultaneous background and analyte measurement, which is important when dealing with complex matrices, such as alloys[5].

This work describes the determination of additives to Al in aluminum alloys at the LME specifications, using the Avio 200 ICP-OES.

Experimental

Samples and Sample Preparation

A general sample preparation for dissolving aluminum alloys[6] involves heating 0.1 g of the alloy in 6 mL of 10M NaOH, followed by the addition of 1 mL of H_2O_2 (30% w/w). The NaOH is required to dissolve the Si in the alloy, while the addition of peroxide drives off any dissolved gas. Next, 25 mL of 1:1 HNO_3 (v/v) and 10 mL of 1:1 HCl (v/v) are added to complete the digestion and keep the dissolved elements in solution. This solution is diluted to 100 mL for analysis.

For this work, solutions were made from single element standards to simulate the dissolution process. The matrix consisted of 5% HNO_3 (v/v) + 3.5% HCl (v/v) + 1.5% NaCl (w/v) + 1% Al (w/v). Although NaCl is not used in sample preparation, it was added to match the sodium content of the digestion procedure. Initially, NaOH was added, but it reacted with the acids to produce dissolved gas, leading to variable results. As a result, NaCl was substituted to match the Na content of the digestion procedure.

To account for the range of concentrations covered by the various specifications, spikes were added to the matrix at the lowest and highest values for each element listed in Table 1. Calibration curves were constructed in the matrix, but the blank consisted of just the acid (5% HNO_3 + 3.5% HCl). All elements were determined with external calibration curves, and Si, Cu, Zn, and Fe were measured against linear bracketing calibration curves to account for the higher accuracy required for these elements. Table 2 reports the calibration standards, calibration equations, and spike levels for each element. Scandium (Sc) was added to all solutions as an internal standard.

Table 1. London Metal Exchange Specifications for Aluminum Alloys.

Element	Aluminum Association: A380.1 Ingot (%)	Secondary Al Alloy: LME/DIN 226 (%)	Japanese Industrial Standard: JIS H 2118:2006:AD 12.1 (%)	North American Special Al Alloy (%)
Si	7.5-9.5	8.0-11.0	9.6-12.0	8.50-9.50
Cu	3.0-4.0	2.0-3.5	1.5-3.5	3.00-3.50
Zn	2.9	1.2	1.0	3.00
Fe	1.0	1.0	0.6-1.0	0.8-1.00
Mn	0.50	0.1-0.4	0.5	0.45
Ni	0.50	0.3	0.5	0.50
Sn	0.35	0.1	0.2	0.10
Mg	0.10	0.1-0.5	0.3	0.10
Ti	---	0.15	0.3	0.10
Pb	---	0.2	0.2	0.10
Cr	---	---	---	0.10

Table 2. Calibrations and Spikes Details.

Element	Calibration Equation	Calibration Standards (mg/L)	Low Spike (mg/L)	High Spike (mg/L)
Si	Linear Bracketing	50; 100; 150	75	120
Cu	Linear Bracketing	10; 25; 50	15	40
Zn	Linear Bracketing	5; 15; 40	10	30
Fe	Linear Bracketing	5; 8; 12	6	10
Ni	Linear, Calc Intercept	0.5; 1; 5	3	5
Mn	Linear, Calc Intercept	0.5; 1; 5	1	5
Mg	Linear, Calc Intercept	0.5; 1; 5	1	5
Sn	Linear, Calc Intercept	0.5; 1; 5	1	3.5
Ti	Linear, Calc Intercept	0.5; 1; 5	1	3
Pb	Linear, Calc Intercept	0.5; 1; 5	1	2
Cr	Linear, Calc Intercept	0.5; 1; 5	1	1

Instrumental Parameters

All analyses were done on the Avio 200 ICP-OES using the conditions reported in Table 3, while wavelengths are shown in Table 4. All measurements were made in radial mode to minimize matrix effects. The wavelengths chosen were interference-free, thereby simplifying the methodology by eliminating the need for interference corrections. For the elements requiring high accuracy, a longer read time (two seconds) was used, resulting in improved precision and accuracy. The other elements were measured with a read-time range of 0.2-1 second. A photo of the plasma aspirating a sample is shown in Figure 1, where the presence of sodium is visible by the bright orange tongue in the center of the plasma.

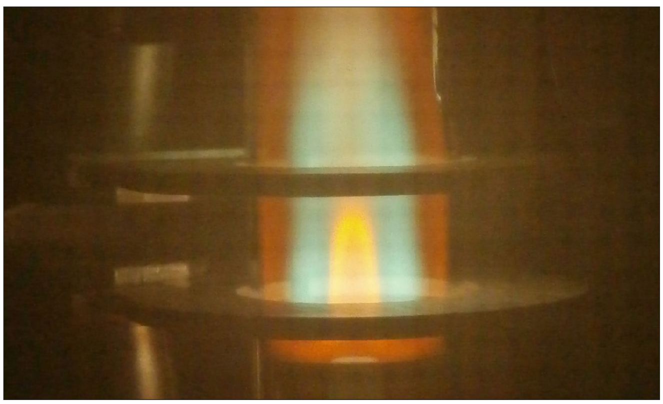

Figure 1. Capture of the plasma on the Avio 200 ICP-OES while nebulizing a sample.

Table 3. Avio 200 ICP-OES Instrumental Parameters.

Parameter	Value
Nebulizer	SeaSpray™
Spray Chamber	Baffled Glass Cyclonic
RF Power	1500 W
Injector	2.0 mm Ceramic
Torch	Quartz, 1 Slot
Plasma Flow	10 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.65 L/min
Torch Position	-3
Sample Uptake Rate	1 mL/min
Replicates	3
Plasma View	Radial

Table 4. Wavelengths and Read Times.

Element	Wavelength (nm)	Read Times (s)
Si	212.412	2
Cu	327.393	2
Zn	206.200	2
Fe	238.204	2
Ni	231.604	0.2-1
Mn	259.372	0.2-1
Mg	285.213	0.2-1
Sn	189.927	0.2-1
Ti	334.940	0.2-1
Pb	283.306	0.2-1
Cr	267.716	0.2-1
Sc (Int Std)	361.383	0.2-1

Results and Discussion

To determine the accuracy of the proposed methodology, the matrix solutions were spiked at both the low and high specification levels, as reported in Table 2, and then analyzed. The experimental results are reported in Figure 2. With recoveries within ± 2% for the majors (Si, Cu, Zn, and Fe) and ± 5% for the other elements, the accuracy of the methodology is established.

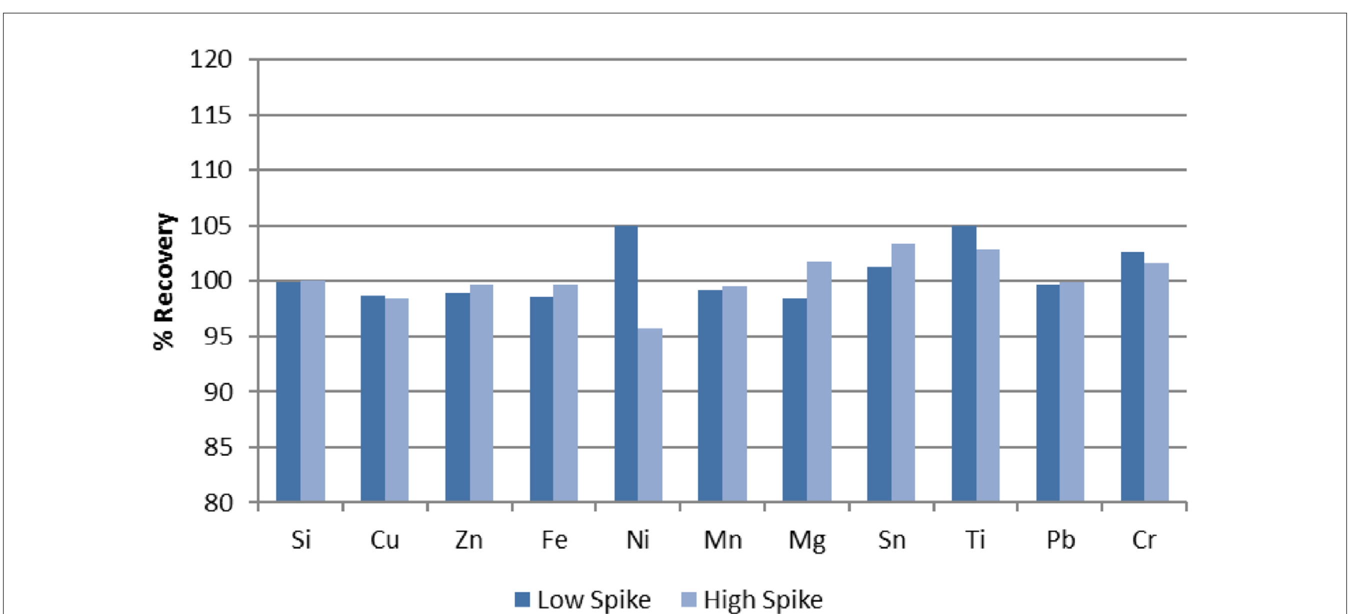

Figure 2. Recoveries of high and low spikes in simulated Al alloy digest covering the range of LME specifications.

To evaluate the stability of the methodology, 10 low and 10 high spike solutions were measured in alternating groups of two over 2.5 hours; the resulting recoveries are shown in Figures 3 and 4. With recoveries for all major elements within 2% and recoveries for the other elements within 6%, the methodology is proven to be stable.

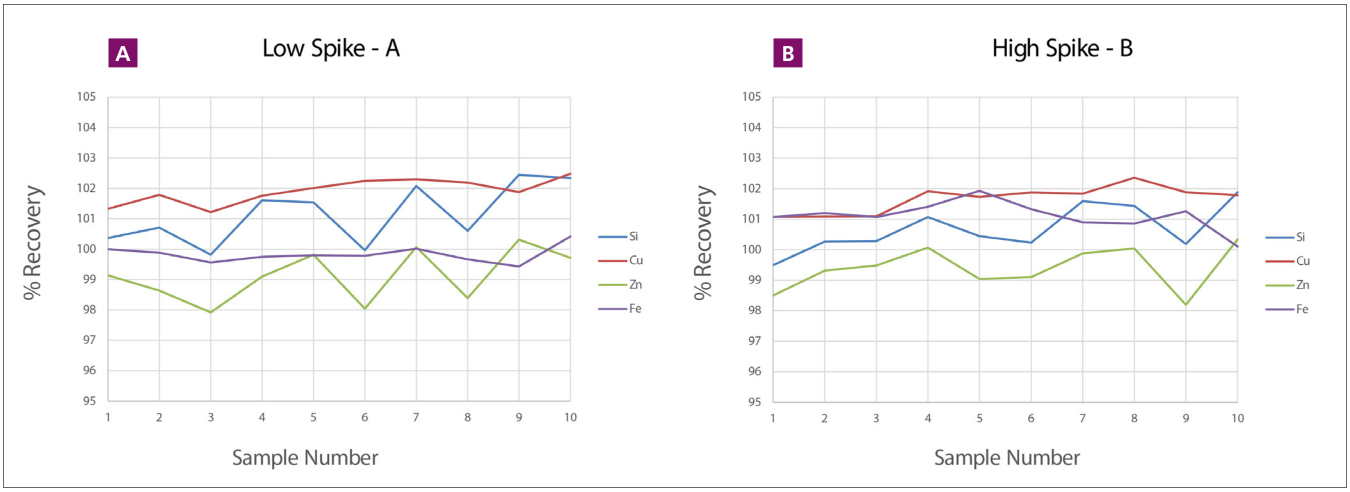

Figure 3. Spike recoveries at LME low (A) and high (B) specifications over 2.5 hours for elements present at 1% weight or higher.

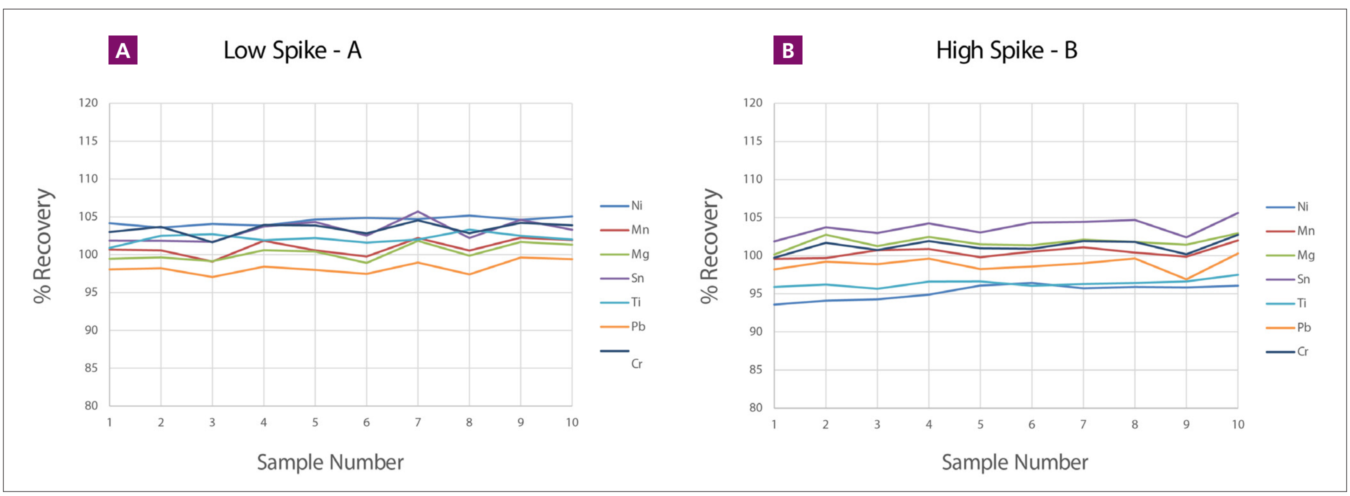

Figure 4. Spike recoveries at LME low (A) and high (B) specifications over 2.5 hours for elements present at less than 1% weight.

Conclusion

This work demonstrates the ability of the Avio 200 ICP-OES to measure analytes in aluminum alloys at both the high and low specifications from the London Metal Exchange. By using linear bracketing calibrations with a longer read time, accuracies of ± 2 % can be obtained for major components in the alloy. The accuracy of the minor components is within ± 5%, using linear calibrations and shorter read times. The methodology has proven to be reliable and stable.

References

1. https://www.aluminum.org/resources/industry-standards/aluminum-alloys-101
2. http://www.aalco.co.uk/datasheets/Aluminium-Alloy_Introduction-to-Aluminium-and-its-alloys_9.ashx
3. "Special Contract Rules for Aluminum Alloy", London Metal Exchange.
4. "Special Contract Rules for North American Special Aluminum Alloy", London Metal Exchange.
5. "Avio 200 ICP-OES Custom-Designed Solid-State Detector", Technical Note, PerkinElmer, 2016.
6. "Aluminum and Aluminum Alloys – Chemical Analysis – Inductively Coupled Plasma Optical Emission Spectral Analysis", (UNI EN 14242) European Committee for Standardization, 2004.

Consumables Used

Component	Part Number
Sample Uptake Tubing: Black/Black (0.76 mm id) PVC, Flared	N0777043
Drain Tubing: Gray/Gray (1.30 mm id), Santoprene	N0777444
Aluminum Standard, 10,000 µg/mL	N9304111 (125 mL) N9304110 (500 mL)
Copper Standard, 10,000 µg/mL	N9304112 (125 mL) N93000283 (500 mL)
Iron Standard, 10,000 µg/mL	N9304113 (125 mL) N9307117 (500 mL)
Silicon Standard, 1000 µg/mL	N9304122 (125 mL)
Zinc Standard, 10,000 µg/mL	N9304129 (125 mL)
Chromium Standard, 1000 µg/mL	N9300173 (125 mL) N9300112 (500 mL)
Lead Standard, 1000 µg/mL	N9300175 (125 mL) N9300128 (500 mL)
Magnesium Standard, 1000 µg/mL	N9300179 (125 mL) N9300131 (500 mL)
Manganese Standard, 1000 µg/mL	N9303783 (125 mL) N9300132 (500 mL)
Scandium Standard, 1000 µg/mL	N9303798 (125 mL) N9300148 (500 mL)
Tin Standard, 1000 µg/mL	N9303801 (125 mL) N9300161 (500 mL)
Titanium Standard, 1000 µg/mL	N9303806 (125 mL) N9300162 (500 mL)
Autosampler Tubes, Case of 500	B0193233 (15 mL) B0193234 (50 mL)

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