APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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High-Precision Analysis of Battery Materials with the Avio 550 Max ICP-OES

Introduction

The use of batteries is growing rapidly as new uses are found, including providing power for anything ranging from consumer products to medical devices to automobiles. Additionally, with the growing use of alternative energy sources, batteries are required to store excess energy and release it when needed.

As a result of this rapid and varied demand, new battery types, technologies, and materials are continuously being developed. Some commonly-used elements in different types of batteries include lithium (Li), manganese (Mn), nickel (Ni), phosphorus (P), and zinc (Zn), among others. The percentage of these components can range from single digit percent up to 30%, depending on the battery.

An important factor in obtaining optimum performance is accurately knowing the ratios of the major components since deviations can negatively affect battery performance, as can the presence of impurities. Therefore, the major components must be measured both with high accuracy and precision, while, at the same time, measuring impurity levels.

ICP-OES is the ideal analytical technique to meet these needs: it has a high tolerance to matrices, yet is capable of high precision and can accurately measure impurities down to the µg/L level. High precision ICP-OES (HP-ICP-OES), only available on fully simultaneous ICP-OES systems like PerkinElmer's Avio® 550 Max, provides unparalleled accuracy, with RSDs of 0.1% or less. HP-ICP-OES compensates for all sources of noise by measuring the internal standard at the same time as the analyte, for fully simultaneous measurements.

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This work demonstrates the Avio 550 Max ICP-OES' ability to measure elements commonly found in batteries with both high precision and accuracy while, at the same time, measuring common impurities.

Experimental

Materials and Sample Preparation

To mimic a digestion of battery materials, standards containing Mn, P, Li, Ni, and Zn were prepared at the concentrations shown in Table 1 in 2% nitric acid (v/v). In addition, common impurities were also added to the solutions containing the major components at the concentrations in Table 1. All the concentrations shown in Table 1 simulate a 100x dilution of starting materials used in batteries. Scandium (Sc) was added to all solutions as an internal standard.

Instrumental Parameters

All analyses were carried out on the Avio 550 Max ICP-OES using the parameters shown in Table 2; the wavelengths, plasma views, and timings are shown in Table 3. For optimum precision with HP-ICP-OES, the internal standards are read with the same integration time as the analytes. The precision was further increased by using a 10-second read time, which allowed more readings to be acquired. The majors were measured against linear bracketing calibration curves, while the impurities were measured with linear-through-zero regressions; all calibration standards were prepared in 2% HNO_3.

Results and Discussion

Calibration curves were constructed, and the middle standard was measured 10 times against the calibration curve. Figure 1 shows that the relative standard deviations (RSDs) for all the major elements in all of the samples was less than or equal to 0.2%, with the majority of results being < 0.1%. This type of precision is only possible when the internal standard is read at the same integration time (0.01 sec) at the exact same time as the analyte. By having true simultaneous measurements, the internal standard corrects for shot and flicker noise, resulting in exceptional precisions.

Table 1. Elements and Concentrations.

Major Components	
Element	**Concentrations (mg/L)**
Mn, P	500, 1000, 2000
Li	125, 250, 500
Ni, Zn	50, 100, 200
Impurities	
Element	**Concentrations (µg/L)**
Cu, Cd, Hg, Mo, Pb	50, 100, 200

Table 2. Instrumental Parameters.

Parameter	Value
Nebulizer	SeaSpray™
Spray Chamber	Baffled Glass Cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1500 W
Injector	2.0 mm id Alumina
Nebulizer Gas Flow	0.65 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	10 L/min
Torch Position	-3
Replicates	3

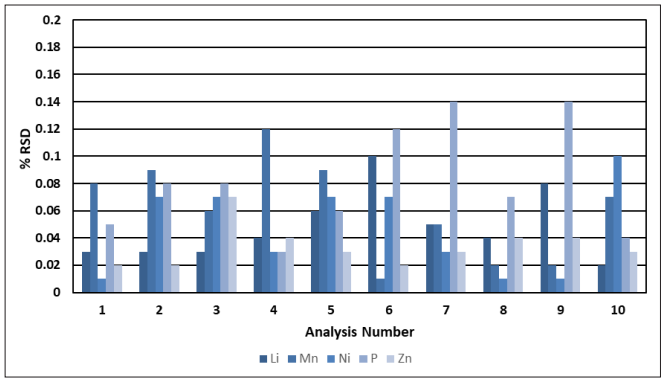

Figure 1. Precision (%RSD) for major elements during 10 analyses of the middle calibration standard (Mn, P = 1000 mg/L; Li = 500 ppm; Ni, Zn = 100 ppm).

Table 3. Method Parameters.

Category	Analyte	Plasma View	Internal Standard	Plasma View Height	Integration Time (s)	Read Time (s)
Majors	Li 610.362	Radial	Sc 361.383	20	0.01	10
	Ni 232.003	Axial	Sc 361.383	15	0.01	10
	Zn 334.501	Axial	Sc 361.383	15	0.01	10
	Mn 347.413	Radial	Sc 361.383	20	0.01	10
	P 213.623	Radial	Sc 361.383	15	0.01	10
Impurities	Cd 214.440	Axial	Sc 361.383	15	0.05	1
	Cu 327.393	Axial	Sc 361.383	15	0.05	1
	Hg 194.168	Axial	Sc 361.383	15	0.05	1
	Mo 202.031	Axial	Sc 361.383	15	0.05	1
	Pb 220.353	Axial	Sc 361.383	15	0.05	1

During the same analysis, the concentrations of both the majors and impurities were measured, with the recoveries for the majors shown in Figure 2 and the impurities in Figure 3. The major elements recovered within 2% of their expected values, while the impurities recovered within 6%.

The stability of the methodology is evidenced by the precision of the 10 analyses of both the major and impurity elements. As shown in Table 4, the RSDs of the major elements is less than 0.2% and less than 2% for the impurity elements. This reproducibility for the major elements is only possible with the use of HP-ICP-OES. The precision for the impurities demonstrates that both HP-ICP-OES and "normal" analyses can be implemented within the same method without sacrificing data quality.

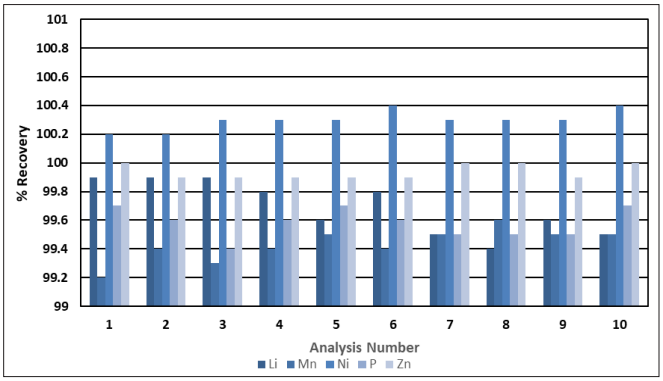

Figure 2. Recovery of major elements over 10 analyses (Mn, P = 1000 mg/L; Li = 500 ppm; Ni, Zn = 100 ppm).

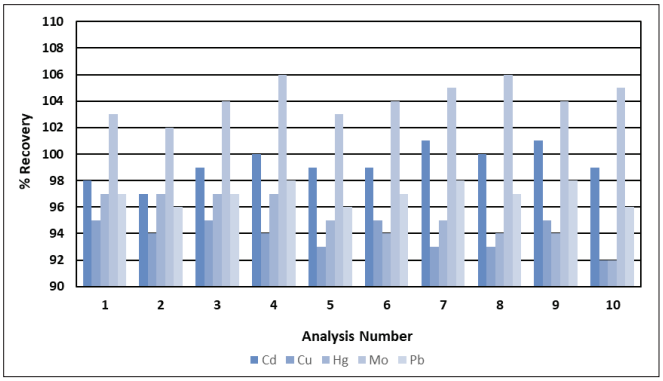

Figure 3. Recovery of minor elements (0.1 mg/L) over 10 analyses.

Table 4. Precision (% RSD) over 10 Analyses of Major and Impurity Elements.

Major Components	
Element	**RSD**
Mn	0.12%
P	0.10%
Li	0.19%
Ni	0.07%
Zn	0.05%
Impurities	
Element	**RSD**
Cu	1.3%
Cd	1.2%
Hg	1.8%
Mo	1.3%
Pb	0.84%

Conclusion

This work demonstrates the ability of the Avio 550 Max ICP-OES to provide extremely high precision using high precision ICP-OES (HP-ICP-OES) made possible only with fully simultaneous measurements of the analytes and internal standards. This ability provides real-time corrections of variations in the analytical signal, resulting in high precisions/low RSDs (typically < 0.10%). Because HP-ICP-OES can be implemented in the same method along with analytes measured conventionally, both matrix components and impurities can be measured together in a single method, as shown in the analysis of matrix components and impurities in common battery materials. When combined with bracketing calibrations, HP-ICP-OES provides both exceptional precision and accuracy in the measurement of matrix materials.

Reference

1. "HP-ICP-OES: Using the Avio 550/560 Max to Achieve the Highest Possible Precisions", Technical Note, PerkinElmer, 2020.

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
Lithium Standard, 10,000 µg/mL	N9304323 (125 mL) N9304324 (500 mL)
Manganese Standard, 10,000 µg/mL	N9304115 (125 mL)
Nickel Standard, 10,000 µg/mL	N9304117 (125 mL) N9304116 (500 mL)
Phosphorus Standard, 10,000 µg/mL	N9304119 (125 mL) N9304118 (500 mL)
Zinc Standard, 10,000 µg/mL	N9304129 (125 mL)
Cadmium Standard, 1000 µg/mL	N9300176 (125 mL) N9300107 (500 mL)

Component	Part Number
Copper Standard, 1000 µg/mL	N9300183 (125 mL) N9300114 (500 mL)
Lead Standard, 1000 µg/mL	N9300175 (125 mL) N9300128 (500 mL)
Mercury Standard, 1000 µg/mL	N9300174 (125 mL) N9300133 (500 mL)
Molybdenum Standard, 1000 µg/mL	N9303784 (125 mL) N9300134 (500 mL)
Scandium Standard, 1000 µg/mL	N9303798 (125 mL) N9300148 (500 mL)
Autosampler Tubes, case of 500	B0193233 (15 mL) B0193234 (50 mL)

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