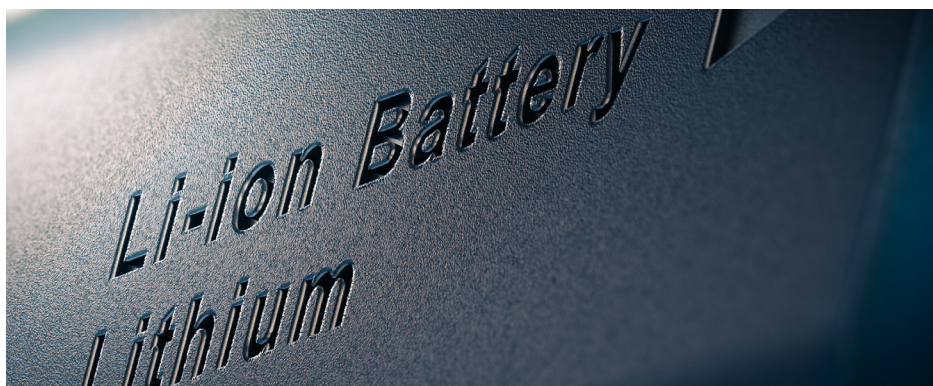


Rapid Analysis of Elemental Impurities in Battery Electrolyte by ICP-OES

Quality control measurement of 12 elements in
lithium hexafluorophosphate



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Introduction

The electrolyte used in lithium-ion batteries acts as a bridge between the positive and negative electrodes, and is therefore fundamental to the operation, performance, and safety of the battery. Due to its conductivity properties, cost, safety, and environmental impact, lithium hexafluorophosphate (LiPF_6) is currently the most used electrolyte in lithium-ion batteries worldwide.

In China, the elements present in the LiPF_6 electrolyte are typically analyzed according to the chemical industry standard "Lithium hexafluorophosphate electrolyte" (HG/T 4067-2015) (1). The standard method uses ICP-OES to analyze all impurities except sulfate, which is determined using a turbidimetric method. While turbidity measurements are low cost, they have high detection limits and are labor intensive. The accuracy and precision of the measurements is often dependent on the skill of the analyst. Also, many ICP-OES instruments used for the long-term analysis of electrolyte samples are prone to a buildup of carbon on the torch, which

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affects instrument stability and data quality. To address these challenges, a highly robust Agilent 5110 vertical dual view (VDV) ICP-OES was used for the measurement of 12 elements in LiPF₆ electrolyte. The element list included: Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, S, and Zn.

Experimental

Instrumentation

The Agilent 5110 VDV ICP-OES was used in this study. The 5110 uses a vertical torch and a solid-state radio frequency (SSRF) system operating at 27 MHz to deliver a plasma with the stability and robustness necessary for the analysis of organic samples. The cooled cone interface (CCI) reduces the formation of interferences, improving the reliability of the analysis results. The 5110 ICP-OES was fitted with an inert sample introduction kit consisting of an inert double-pass spray chamber, OneNeb nebulizer, Easy-fit torch, and solvent resistant sample and waste pump tubes. All measurements were performed in axial plasma viewing mode, as only trace level elements were of interest.

Instrument operating conditions are given in Table 1.

Table 1. ICP-OES operating conditions.

Parameter	Setting
Torch	Easy-fit inert demountable VDV torch for HF digests, with 1.8 mm id ceramic injector
Nebulizer	Inert OneNeb series 2 concentric
Spray Chamber	Inert double-pass spray chamber
Read Time (s)	10
Replicates	3
Stabilization Time (s)	8
Fast Pump (rpm)	60
Pump Speed (rpm)	10
Power (kW)	1.4
Plasma Gas Flow (L/min)	12
Auxiliary Gas Flow (L/min)	1.0
Nebulizer Gas Flow (L/min)	0.55
Viewing Mode	Axial

Background correction

The Agilent fast automated curve-fitting technique (FACT) was used to minimize spectral interferences on aluminum (Al) and arsenic (As) arising from carbon species present in the organic solvent and to improve detection limits (DLs). Figure 1 shows the results for As before and after FACT correction.

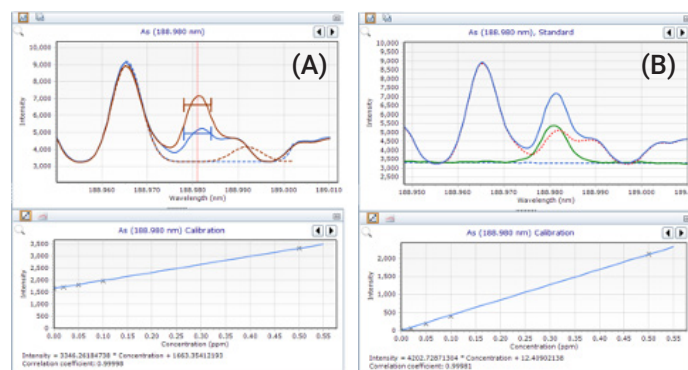


Figure 1. (A) Top left overlaid spectra of 20% ethanol and 0.5 ppm As standard in 20% ethanol using Fitted BC. The blue trace is a 20% ethanol blank and the brown trace is a 0.5 ppm As standard. The graph (bottom left) is an As calibration curve before FACT correction - showing a large offset at the origin. (B) Top right is a FACT deconvolution of an As 0.5 ppm standard. The lower graph is the calibration curve for As after FACT correction. The curve goes through the origin.

Reagents, standards, and samples

High-purity anhydrous ethanol was bought from Sigma-Aldrich. Agilent standards were used, including a 10 mg/L multi-element standard solution 2A, 1000 mg/L mercury standard solution, and 1000 mg/L sulfur standard solution. High purity de-ionized water (DIW) was prepared by a Millipore Milli-Q ultrapure water system. Two commercial electrolytes (Sample A and Sample B) were bought for the study.

Standard and sample preparation

A 20% (w/w) aqueous solution of ethanol was used as a blank solution and diluent. As the LiPF₆ electrolyte contained carbonate, it was diluted 10–20 times by weight in the diluent. Excess carbonate can cause instability in emission signals due to deposits building up on the torch's injector. To prepare the sample, 5 g of electrolyte was accurately weighed, and 20% ethanol was added to a final weight of 100 g. A series of standard solutions (0.02, 0.05, 0.1, and 0.5 mg/L) were prepared by weight.

Results and discussion

Calibration

Linear calibrations were obtained for all 12 analytes from 0.02 to 0.5 mg/L. Calibration coefficients for all elements were greater than 0.999, as shown in Table 2.

Table 2. Calibration correlation coefficients for 12 elements.

Element and Wavelength (nm)	Correlation Coefficient	Element and Wavelength (nm)	Correlation Coefficient
Al (396.152)	0.9999	Fe (238.204)	1.0000
As (188.980)	0.9998	Mg (279.553)	1.0000
Ca (396.847)	0.9999	Ni (231.604)	0.9999
Cd (214.439)	1.0000	Pb (220.353)	0.9997
Cr (205.560)	0.9998	S (180.669)	0.9990
Cu (327.395)	0.9999	Zn (213.857)	0.9999

Method detection limits

The three sigma method detection limits (MDLs) were based on 11 replicate measurements of the digestion blank solution taken during the analytical run. The MDLs in Table 3 were calculated based on sample preparation (5 g sample to 100 g final weight).

Table 3. Method detection limits.

Element and Wavelength (nm)	MDL (mg/kg)	Element and Wavelength (nm)	MDL (mg/kg)
Al (396.152)	0.06	Fe (238.204)	0.06
As (188.980)	0.21	Mg (279.553)	0.03
Ca (396.847)	0.16	Ni (231.604)	0.03
Cd (214.439)	0.04	Pb (220.353)	0.1
Cr (205.560)	0.05	S (180.669)	0.25
Cu (327.395)	0.04	Zn (213.857)	0.04

Quantitative analysis and spike recovery test

Quantitative results for 12 elements in electrolyte A and electrolyte B are shown in Table 4. Since only Ca, S, and Zn were measured above the MDL in both samples, electrolyte B was spiked with each element at 0.025 mg/L. The measured S concentration in both electrolyte samples was above the highest calibration standard, so the spike recovery was not determined.

The results in Table 4 show that the spike recoveries for all the other elements ranged from 90 to 110%. The spiked sample was analyzed seven times. Although the elemental concentration in the test solution was low (0.025 mg/L), the percent relative standard deviation (RSD) of each element was < 3.1%. The precision of the recovery test results demonstrates the suitability of the 5110 ICP-OES method for the determination of elemental impurities in LiPF₆ electrolyte.

Table 4. Calibration correlation coefficients for 12 elements.

Element and Wavelength (nm)	Electrolyte Sample A	Electrolyte Sample B			
	Measured Concentration (mg/kg)	Measured Concentration (mg/kg)	Spiked Measured Concentration (mg/kg)	Spike Recovery (%)	RSD (%)
Al (396.152)	<MDL	<MDL	0.54	108	2.7
As (188.980)	<MDL	<MDL	0.54	108	3.1
Ca (396.847)	0.71	0.53	1.07	108	1.5
Cd (214.439)	<MDL	<MDL	0.49	98	2.1
Cr (205.560)	<MDL	<MDL	0.51	101	2.0
Cu (327.395)	<MDL	<MDL	0.51	102	1.5
Fe (238.204)	<MDL	<MDL	0.51	102	1.6
Mg (279.553)	<MDL	<MDL	0.52	103	1.5
Ni (231.604)	<MDL	<MDL	0.50	99	1.6
Pb (220.353)	<MDL	<MDL	0.46	92	2.6
S (180.669)	2412	9070	ND	ND	ND
Zn (213.857)	0.3	0.17	0.69	104	1.3

ND = not determined

Conclusion

The study has shown that the Agilent 5110 VDV ICP-OES is suitable for the quality control of elemental impurities in electrolytes containing lithium and fluorine, such as lithium hexafluorophosphate. The instrument's SSRF generator and vertical torch, combined with the CCI, provide the matrix tolerance and stability that is required for the routine analysis of organic samples.

Following a simple sample preparation procedure where the LiPF₆ electrolyte was diluted with 20% aqueous ethanol solution, sub-mg/kg MDLs and spike recoveries (90–110%) were achieved for the target elements. The robustness of the instrument's sample introduction system prevented any buildup of carbon on the torch.

The 5110 ICP-OES multi-element method included sulfur, which enabled the concentration of sulfate in the electrolyte to be determined without the need for a separate measurement. Using ICP-OES to measure sulfate rather than using a traditional turbidimetric method simplifies the application, speeds up the analysis, and improves the quality of the data.

References

1. Chinese Standard HG/T 4067-2015 lithium hexafluorophosphate electrolyte, accessed April 2020, <https://www.chinesestandard.net/PDF/English.aspx/HGT4067-2015>



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