Determination of elemental impurities in lithium iron phosphate using ICP-OES

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Keywords: Lithium iron phosphate, iCAP PRO ICP-OES, lithium battery, cathode material

Goal

This application note describes the analysis of lithium iron phosphate using the Thermo Scientific™ iCAP™ PRO Series ICP-OES. The note describes the method development as well as presenting key figures of merit, such as detection limits and stability.

Introduction

Lithium iron phosphate has properties that make it an ideal cathode material for lithium-ion batteries. The material is characterized by a large discharge capacity, low toxicity, and low cost. The first large capacity lithium iron phosphate battery was produced in China in 2005, and the life cycle performance characteristics of the battery were unmatched by other batteries of a similar classification. An ideal application for batteries with a lithium iron phosphate cathode is in series in electric vehicles where frequent charging and discharging of the batteries takes place.

The purity of the cathode material is critical, and changes in the raw material processing and synthesis can cause the introduction of impurities in the final cathode material. These impurities impact the lifetime and energy storage capacity of the battery, and in extreme cases may affect the integrity of the crystal structure of the battery, causing safety issues. Therefore, accurate analysis of the cathode material is key to the performance and safety of lithium batteries made using these materials.

Experimental

Sample and standard preparation

The sample (customer supplied) was weighed (0.2000 g) into a polytetrafluoroethylene beaker. Perchloric acid (10 mL, concentrated) was added, and the beaker was heated on a hot plate until the sample was completely dissolved. When cooled, the sample was transferred to a volumetric flask (50 mL); a blank was prepared using the same method. This solution was analyzed directly to determine elemental impurities. For the matrix elements, a further dilution (factor of 50) with ultrapure water was carried out prior to analysis.

Standards were prepared by diluting stock solutions (1,000 mg/L) to the required concentrations. For impurity analysis, these were 0.05, 0.10, 0.50, and 1.0 mg/L, and, for the matrix elements, these were 2, 5, 10 mg/L for Li, and 10, 20, 50 mg/L for P and Fe.

Instrument, method development, and analysis

The Thermo Scientific iCAP PRO Radial ICP-OES instrument, fitted with a fully demountable extended matrix tolerance (EMT) quartz torch, was used for the analysis. This instrument is ideal for the analysis of complex matrix samples, such as lithium iron phosphate, due to the pre-optimized radial view. The iCAP PRO ICP-OES has continuous wavelength coverage from 167 to 852 nm. Combined with the CID detection of 2,048 × 2,048 pixels, this allows the spectral line library to have more than 50,000 optional spectral lines. Therefore, the iCAP PRO ICP-OES can flexibly use a variety of other spectral lines to avoid interference.

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used to create a LabBook and control the instrument. Wavelengths were selected in the LabBook based on their potential to be free from interferences, method parameters were set (Table 1), and the analysis was carried out. The instrument was calibrated, the unknown samples determined, spikes of the impurity elements (at 0.2 mg/L) were analyzed, and a two-hour stability test was carried out for the matrix elements, measuring one sample every two hours. After the data collection, the sub-array spectrum overlay function was used to examine the spectra of each wavelength. This can be used to determine if any interferences are present and optimize the central integration area and background correction points.

Results and discussion

Calibrations with excellent linearity were obtained for all 26 elements analyzed, as shown in Table 2. For the 23 impurity elements, the concentrations found in the sample (corrected for the dilution factor) ranged from below the detection limit of the method for Cd, Mo, Se, and W up to 240 mg/kg for Mn (Table 3). Detection limits achieved for the impurity elements were in the µg/L range in the solutions measured and in the sub-mg/kg to low mg/kg range for the solid sample (Table 3). Spike recoveries for the impurity elements (all spiked at 0.2 mg/L) ranged from 90 to 110% of the spiked concentration, as shown in Figure 1. Finally, excellent precision (<0.8% RSD over seven repeat analyses) was achieved for the 2-hour measurement stability test of the matrix elements Li, Fe and P (Table 4).

Table 1. Instrument parameters used for the analysis

Parameter	Setting
Instrument model	iCAP PRO Radial
Observation method	Radial
Plasma torch	Demountable EMT torch
Injector	2.0 mm quartz injector
Spraychamber	Glass concentric
Nebulizer	Glass concentric
Peristaltic pump speed	50 rpm
Plasma RF power	1,150 W
Nebulizer gas flow	0.6 L/min
Auxiliary gas flow	0.5 L/min
Cool gas flow	12 L/min

Table 2. Correlation coefficient R^2 of the standard curve of each element

Element and wavelength (nm)	R^2	Element/wavelength (nm)	R^2
Al 396.152	0.9997	Na 589.592	0.9999
As 189.042	0.9999	Ni 231.604	0.9999
Ba 455.403	0.9999	P 177.495	0.9997
Ca 393.366	0.9999	Pb 168.216	1.0000
Cd 228.802	0.9999	S 180.731	1.0000
Co 228.616	0.9999	Sb 206.833	0.9999
Cr 206.157	0.9999	Se 196.090	0.9991
Fe 271.441	0.9999	Si 212.412	0.9999
K 766.490	0.9996	Sn 189.989	1.0000
Li 670.791	0.9996	Ti 323.452	1.0000
Mg 285.213	0.9999	V 309.311	0.9998
Mn 257.610	0.9999	W 207.911	1.0000
Mo 202.030	1.0000	Zn 213.856	0.9999

Table 3. Impurity elements test results: the detection limit of the method is based on the weighed sample (0.2 g) and the constant volume of 50 mL; ND = not detected

	Sample (mg/kg)	Solution detection limit (µg/L)	Method detection limit (mg/kg)
Al 396.152	110.08	6.18	1.54
As 189.042	6.16	11.21	2.8
Ba 455.403	0.55	0.19	0.05
Ca 393.366	37.23	0.09	0.02
Cd 228.802	ND	1.45	0.36
Co 228.616	7.51	2.09	0.52
Cr 206.157	8.19	2.2	0.55
K 766.490	21.94	35.87	8.97
Mg 285.213	119.54	0.71	0.18
Mn 257.610	240.22	0.21	0.05
Mo 202.030	ND	2.46	0.62
Na 589.592	167.64	34.79	8.70
Ni 231.604	2.69	2.24	0.56
Pb 168.216	9.48	20.8	5.2
S 180.731	24.54	7.69	1.92
Sb 206.833	20.54	13.35	3.34
Se 196.090	ND	15.48	3.87
Si 212.412	13.76	11.29	2.82
Sn 189.989	1.38	3.21	0.8
Ti 323.452	228.11	0.56	0.14
V 309.311	17.78	1.37	0.34
W 207.911	ND	9.91	2.48
Zn 213.856	97.98	0.53	0.13

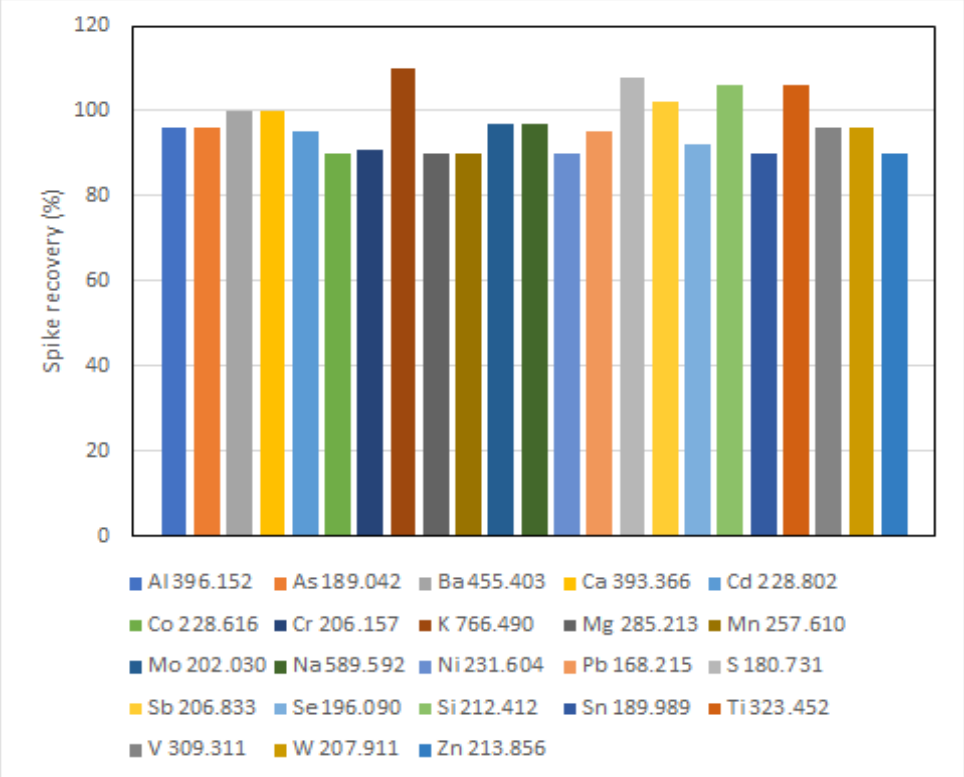

Figure 1. Spike recovery results for samples spiked with 0.2 mg/L of the 23 impurity elements

Table 4. Results of matrix elements analysis and 2-hour stability test (measured every 20 minutes for 2 hours, 7 times in total, unit %)

	Measured concentration (mg/L)		
Sample/element	**Fe 271.441 nm**	**P 177.495 nm**	**Li 670.791 nm**
1–1	34.69	19.33	4.42
1–2	34.87	19.55	4.44
1–3	34.67	19.48	4.43
1–4	34.47	19.51	4.41
1–5	34.33	19.47	4.37
1–6	34.63	19.62	4.43
1–7	34.20	19.47	4.35
Average value	34.55	19.49	4.41
Standard deviation	0.23	0.09	0.03
Relative standard deviation %	0.66	0.46	0.76

Conclusion

This application note demonstrates the effective application of the iCAP PRO Radial ICP-OES instrument for analysis of elemental impurities in lithium iron phosphate, a commonly used cathode material in lithium-ion batteries. A total of 23 key impurity elements were accurately and sensitively measured, as demonstrated by the results obtained for the customer supplied sample and the quantitative spike recoveries obtained for each element spiked into the sample. The instrument not only has the capability to measure elemental impurities at low concentrations, but also has the linear range to determine matrix elements accurately over a typical analysis sequence, as demonstrated by the high precision results achieved for the matrix element stability test. Use of the robust, fully demountable EMT torch design for this application ensures low operating consumable costs and this, coupled with excellent stability and sensitivity, makes the iCAP PRO ICP-OES an ideal choice for accurately measuring a range of matrix and impurity elements in materials for the lithium battery industry.

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