APPLICATION NOTE   73872

Sensitive determination of elements in lithium batteries using the Thermo Scientific iCAP PRO XP ICP-OES

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Goal
This note demonstrates a fast analytical method for the determination of major and trace elements in the ternary cathode material of lithium batteries using the Thermo Scientific™ iCAP™ PRO Series ICP-OES.

Introduction
The continuous development of lithium-ion batteries and the research into their materials is at the forefront of the energy sector as it moves away from fossil fuels. To regulate the quality of production, the Chinese national standard method YS/T 798-2012 was established. All new lithium battery developments must meet the requirements of these standards. The ternary material of lithium batteries typically contains lithium, nickel, cobalt, and manganese, and potassium aluminate as its cathode material. In recent years, lithium batteries using ternary materials as cathode materials have gradually replaced nickel-metal hydride batteries, lithium cobalt batteries and lithium-ion phosphate batteries. This is due to the high capacity, good cycle
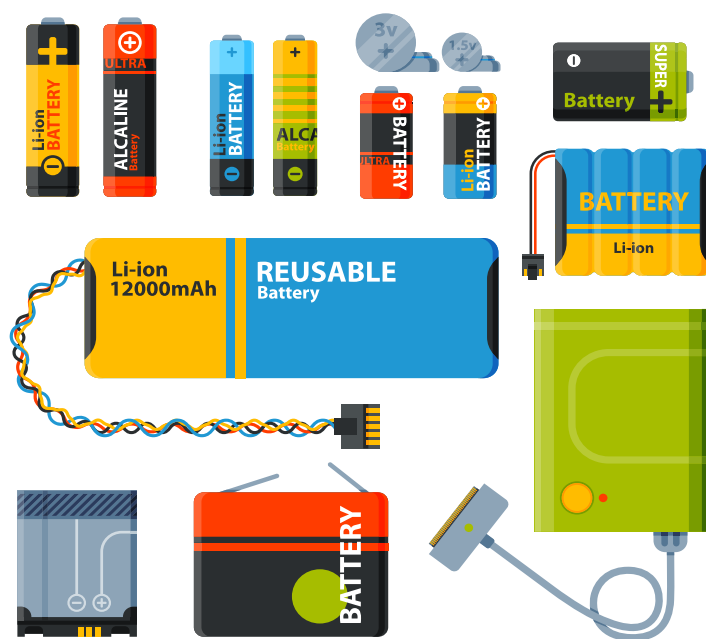
stability (battery life), and moderate cost of the new battery type. The proportion and content of the main elements in the ternary cathode material can affect the performance and cost of the lithium battery significantly and the content of impurities in the ternary material alters the safety of the battery. Therefore, the accurate determination and quantification of the main elements, as well as trace impurities in the ternary cathode material, becomes particularly important.

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Experimental

Standards and sample preparation

A series of calibration standards were prepared to determine the elemental impurities and major elements within the lithium battery material. Multi-element standard solutions were prepared by diluting single-element stock standards with 2% hydrochloric acid (elements in this solution are listed in Table 2, on page 3). The standard concentrations of analytes defined as impurities were 0, 0.05, 0.10, 0.50, 1.0, and 5.0 mg·L^{-1} in a mixed standard solution To determine the concentration of major elements, calibration standards containing lithium at 0, 2, 5, and 10 mg/L and Co, Ni, and Mn at 0, 10, 20, and 50 mg/L were prepared.

To prepare the sample, an aliquot of 0.25 g of ternary cathode material was weighed into a polytetrafluoroethylene beaker. A volume of 10 mL hydrochloric acid (37%, Sinopharm) was added, and the mixture was heated on a hot plate for digestion at just below the boiling point of the acid until all the sample powder dissolved to a clear solution. After the sample cooled, it was transferred to a 50 mL volumetric flask and filled to volume with ultrapure water with a resistivity of 18.2 MΩ·cm (Barnstead™ water purification system, Thermo Scientific™) A preparation blank was also prepared using the same method. For the analysis of elemental impurities, the sample solution was analyzed undiluted, while for the analysis of major elements, the sample solution was diluted 50-fold.

Instrument parameters and method optimization

The iCAP PRO XP ICP-OES Radial system was selected for the application, the lower detection limits offered by the axial view of a dual view system were not required for

Table 1. Instrument parameters used for the analysis

Parameter	Setting
Peristaltic pump speed	50 rpm
RF power	1150 W
Nebulizer gas	0.6 L·min^{-1}
Auxiliary gas	0.5 L·min^{-1}
Cooling gas	12 L·min^{-1}
Viewing mode	Radial
Nebulizer	Glass concentric nebulizer
Torch	EMT quartz torch
Injector	2.0 mm quartz injector
Spraychamber	Glass cyclonic spraychamber
Radial viewing height	10 mm
Exposure time	10 s
Analysis mode	iFR

this application. The system utilizes intelligent Full Range (iFR) mode and captures the complete spectrum in the range of 167 to 852 nm in one exposure. This not only reduces the overall analysis time, but also the operational cost as the argon gas consumption is also reduced. The parameters used for the analysis are shown in Table 1. The standard and the sample solutions were introduced into the plasma to collect the spectral data information of all elemental impurities. After data collection was completed, each spectrum was displayed by the subarray spectrum overlay functionality of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software (Figure 1). Using the wavelength library in the Qtegra ISDS Software, potential interferences can be avoided. The adjustment and optimization of the array position allows for more reasonable data collection points.
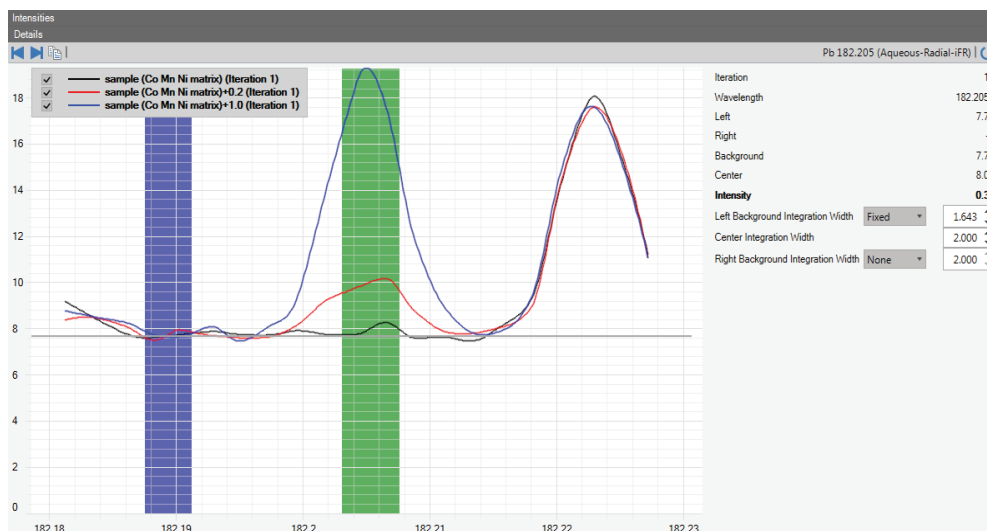

Figure 1. Spectrum of Pb at 182.205 nm, showing no interference in the central observation area

Results and discussion

The correlation coefficients R^2 of the obtained calibration curves were higher than 0.9995 for all analytes, indicating excellent linearity of the wavelengths selected (Table 2).

Table 2. Correlation coefficients (R^2) determined from calibration curves of each analyte and concentration range.

Element and wavelength (nm)	Correlation coefficient R^2	Concentration range (mg·L^{-1})
Al 396.152	0.9997	0–5
As 189.042	>0.9999	0–5
Ba 455.403	>0.9999	0–5
Ca 393.366	>0.9999	0–5
Cd 214.438	>0.9999	0–5
Cr 206.157	>0.9999	0–5
Cu 324.754	>0.9999	0–5
Fe 259.940	>0.9999	0–5
K 766.490	0.9995	0–5
Mg 285.213	>0.9999	0–5
Mo 204.598	>0.9999	0–5
Na 589.592	0.9995	0–5
P 213.618	>0.9999	0–5
Pb 182.205	0.9995	0–5
S 180.731	>0.9999	0–5
Sb 206.833	>0.9999	0–5
Si 212.412	0.9995	0–5
Sn 189.989	>0.9999	0–5
Ti 334.941	>0.9999	0–5
V 309.311	>0.9999	0–5
Zn 206.200	>0.9999	0–5
Li 670.791	>0.9999	0–10
Mn 191.510	>0.9999	0–50
Ni 221.647	>0.9999	0–50
Co 228.616	>0.9999	0–50

The unspiked ternary cathode material sample was analyzed for impurities and the results are shown in Table 3.

The sample was spiked with 1.0 mg·L^{-1} of Al and S and 0.2 mg·L^{-1} of all other elements. The recoveries are all in the range of 90% to 110% as shown in Figure 2.

Table 3. Quantification of detected elemental impurities in an unspiked ternary cathode sample as well as instrument and method detection limits. <LOD stands for values below the detection limit.

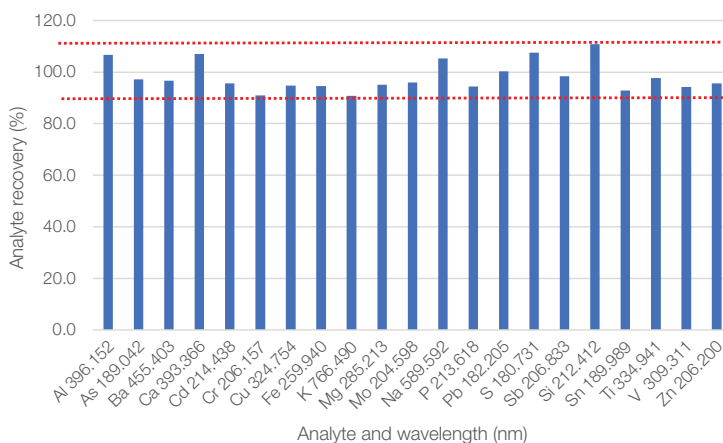| Element and wavelength (nm)	Concentration in the solid sample (mg·kg^{-1})	Instrument detection limit in solution (mg·L^{-1})	Method detection limit in solid (mg·kg^{-1})
Al 396.152	1067	0.0098	1.959
As 189.042	2.06	0.0082	1.631
Ba 455.403	19.16	0.0001	0.020
Ca 393.366	62.13	0.0001	0.010
Cd 214.438	0.37	0.0003	0.064
Cr 206.157	1.26	0.0015	0.304
Cu 324.754	1.64	0.0025	0.500
Fe 259.940	18.62	0.0012	0.243
K 766.490	30.85	0.0090	1.808
Mg 285.213	103	0.0006	0.124
Mo 204.598	<LOD	0.0052	1.035
Na 589.592	102	0.0052	1.030
P 213.618	<LOD	0.0054	1.088
Pb 182.205	7.02	0.0142	2.838
S 180.731	805.39	0.0073	1.461
Sb 206.833	<LOD	0.0192	3.835
Si 212.412	65.39	0.0102	2.039
Sn 189.989	2.41	0.0065	1.296
Ti 334.941	4.54	0.0008	0.166
V 309.311	<LOD	0.0014	0.275
Zn 206.200	1.19	0.0007	0.147

Figure 2. Calculated recoveries (%) for target analytes in the spiked ternary material samples. Spiked at 1.0 mg·L^{-1} for Al and S and with 0.2 mg·L^{-1} for all other elements.

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A stability test was conducted on the major elements in the sample by analyzing the stability test sample every 20 minutes over a period of 2 hours. The RSDs are well below 1% for all analytes and no drift is observed (Table 4).

Table 4. Major element concentration (in mg·kg⁻¹), average values, standard deviation (SD) values as well as repeatability data as % RSD (n=7) of the test sample

Measurement Nr/Element	Li 670.791	Mn 191.510	Ni 221.647	Co 228.616
1	6.99	11.06	34.56	12.33
2	7.01	11.08	34.07	12.16
3	6.95	11.24	34.54	12.34
4	7.06	11.20	34.66	12.34
5	7.05	11.17	34.62	12.29
6	7.03	11.11	34.43	12.34
7	6.98	11.21	34.81	12.46
Average	7.01	11.15	34.53	12.32
SD	0.040	0.068	0.234	0.089
RSD%	0.574	0.613	0.677	0.721

Conclusion

In this application note, a Thermo Scientific iCAP PRO XP ICP-OES Radial system was used to establish a rapid detection method for the determination of major elements and trace impurities in a ternary cathode material used in lithium batteries.

For the impurity elements, recovery values of between 90% and 110% were achieved, as calculated from the spiked samples. For interferences from complex matrices, such as cobalt-nickel-manganese-lithium matrix and the spectral interference of elements, such as nickel and manganese, the iCAP PRO XP ICP-OES system uses a high-resolution optical system that can obtain accurate test results for each element.

All performance specifications meet the testing requirements specified by the national standard method YS/T 798-2012.[1] The iCAP PRO XP ICP-OES system has an ultra-high sensitivity and stability for the detection of elements with characteristic wavelengths in the far ultraviolet region (e.g., S 180.731 nm, Pb 182.205 nm).

The iCAP-PRO XP ICP-OES system performance for major elements, such as nickel, cobalt, manganese, and lithium, demonstrated excellent levels of precision (with % RSD <1%) and accuracy (spike recoveries with the range 90% to 110%).

Overall, the analytical solution employed in this study with the iCAP PRO XP ICP-OES system meets all analytical requirements for routine or research laboratories that aim to analyze elements in ternary materials of lithium batteries.

Reference

1. YS/T 798-2012: China National non-ferrous metal industry standards, Lithium nickel cobalt manganese oxide, Ministry of Industry and Information Technology of the People's Republic of China.

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