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Application News

Inductively Coupled Plasma Atomic Emission Spectrometer ICPE-9800 Series

Major Component and Elemental Impurity Analysis of Lithium-Ion Cathode Materials Using the ICPE-9820

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User Benefits

- The system uses a mini torch that consumes less argon, thus reducing running costs.
- Measurements are stable with minimum long-term and daily fluctuations.
- Post-measurement addition of elements and wavelengths is simple, enabling quantification at optimal wavelengths without re-measurement.

■ Introduction

Lithium-ion secondary batteries (LIBs) are used in many products, such as smartphones and electric vehicles, because they are small and lightweight yet offer high capacity or energy density. However, there is a risk of ignition and heat generation, makes ensuring safety a critical issue. The elemental composition of cathode materials is known to be one of the most important factors that affect energy density and safety. In this Application News, the main elements and impurity elements of LIBs cathode material were analyzed using the ICPE-9820 (Fig. 1). Validation tests on the analysis values and stability tests (2.5 hours variation, 5 days daily variation) on the main components were performed.

Fig. 1 ICPE-9820

■ Sample

$LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ (LIBs cathode materials)

■ Sample Pretreatment

The sample pretreatment procedure is shown in Fig. 2.

Approximately 0.5 g of the sample was weighed, 2 mL of nitric acid and 4 mL of hydrochloric acid were added, and the sample was decomposed (230 °C, 15 min) in a microwave digestion system. After cooling the decomposition vessel to room temperature, the decomposition solution was diluted to a final volume of 50 mL with pure water to obtain the sample stock solution.

- **Sample for Major Components Analysis**

A 0.5 mL aliquot of the sample stock solution was taken, 0.5 mL of nitric acid and hydrochloric acid were added. The sample stock solution and acid were diluted to a final volume of 50 mL with pure water to make analytical samples for major components analysis (diluted 10,000 times). As an internal standard element, Y was added to the solution to 1 mg/L.

- **Sample for Elemental Impurities Analysis**

A 5 mL aliquot of the sample stock solution was taken, and 0.5 mL of nitric acid and hydrochloric acid were added. The sample stock solution and acid were diluted to a final volume of 50 mL with pure water and used as an analytical sample for elemental impurity analysis (diluted 1000 times).

- **Method Blank**

To confirm the amount of contamination of each element during the decomposition process, a processing blank containing no test sample was prepared using the same procedure as the sample for elemental impurity analysis.

- **Sample for Spike Recovery Test**

To confirm the validity of elemental impurity analysis, 0.5 mL of the sample stock solution was taken, 0.5 mL of nitric acid and hydrochloric acid were added. Commercially available standard solutions were added. The solution was diluted to a final volume of 50 mL with pure water.

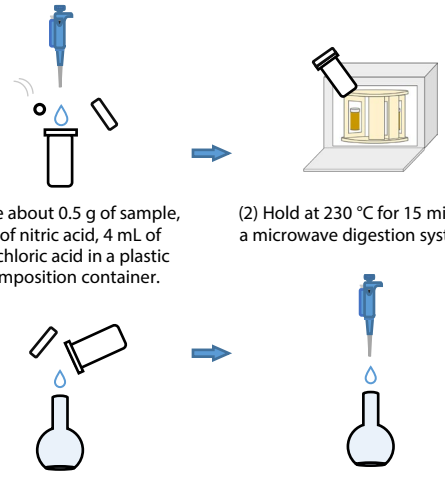


Fig. 2 Sample Pretreatment Procedure

■ Instrument Configuration and Analysis Conditions

Table 1 shows the Instrument configuration. To reduce running costs, the analysis was performed using a mini torch with a lower argon consumption compared to a conventional torch.

The analysis conditions are shown in Table 2. Both axial and radial view were used in this application.

Axial view have the advantage of higher sensitivity compared to radial view. On the other hand, axial view are more susceptible to ionization interference than radial view, which only observe the plasma's high-temperature region, resulting in a narrower concentration range.

For example, the calibration curves of Li for axial and radial view are shown in Fig. 3. The axial view is more sensitive, but the linearity is poor in the high-concentration region.

Therefore, radial view was used to analyze major components in the high-concentration region, and axial view was used to analyze elemental impurities in the trace-concentration region.

Table 1 Instrument Configuration

Instrument:	ICPE-9820
Nebulizer:	Nebulizer, 10UES
Chamber:	Cyclone Chamber, HE
Torch:	Mini-Torch
Auto Sampler:	AS-10

Table 2 Analysis Conditions

RF Power:	1.20 kW
Plasma Gas Flowrate:	10.0 L/min
Auxiliary Gas Flowrate:	0.60 L/min
Carrier Gas Flowrate:	0.70 L/min
View Direction:	Axial / Radial

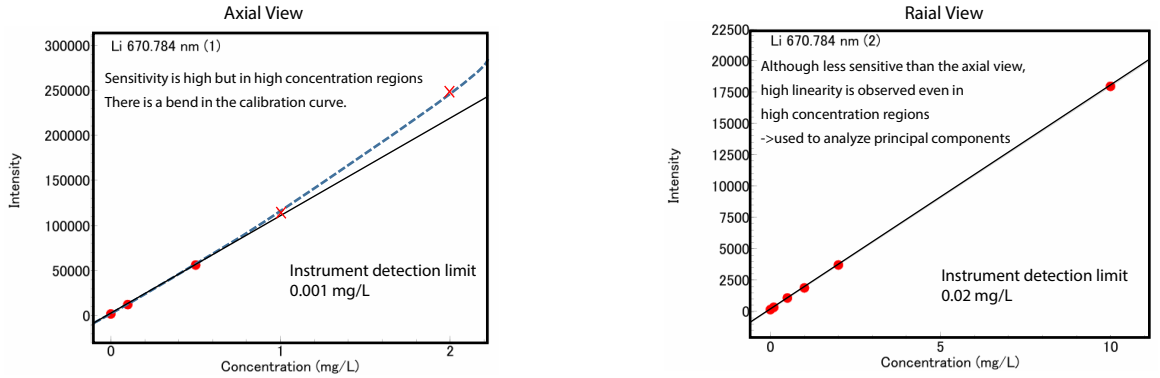


Fig.3 Calibration Curve for Li

■ Standard Sample for Major Components Analysis

Calibration curve samples were prepared by mixing commercially available standard solutions and adding nitric and hydrochloric acid at 1 % each. The concentrations of the measured elements in each calibration curve sample are shown in Table 3. Y was added as an internal standard element to the solutions at 1 mg/L to improve the analytical precision.

Table 3 Concentrations of Calibration Standards for Major Components

Element	STD1 (mg/L)	STD2 (mg/L)	STD3 (mg/L)	STD4 (mg/L)	STD5 (mg/L)	STD6 (mg/L)
Li	0	1	2	10		
Co, Ni, Mn	0			10	20	30
Y	1					
Nitric acid	1 v/v%					
Hydrochloric acid	1 v/v%					

■ Quantitative Results of Major Components

Calibration curves were prepared using the samples in Table 3, and the main components in the cathode material were quantitatively analyzed. The ICPE-9820 has a low sensitivity mode, a high sensitivity mode, and a wide range mode that automatically selects the most suitable mode as the exposure condition. In the analysis of the main components, the internal standard elements and the analytical elements were all measured in the same mode (low sensitivity mode) to increase the simultaneity of measurement and improve accuracy.

Quantitative results are shown in Table 4. The analyses of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ were all close to the theoretical values calculated from the composition ratio.

■ Stability of Major Components Analysis

To confirm the accuracy of the method, the long-term and daily variations of the major components were checked. Analytical stability was also confirmed for the molar ratio of Li/ (Co + Ni + Mn), which is known to be an important factor in LIBs performance.

As for the long-term variation, the variation in the concentration of major components for 2.5 hours of continuous analysis was checked. Results are shown in Fig 4. When the average value was set to 100 %, the variation was between 98 to 102 % and the relative standard deviation was less than 1 %. The results are shown in Table 5.

The daily variation was evaluated by relative standard deviation of accuracy based on measurements taken over five days. The results here were also good, with all of them being less than 1 %.

Table 5 Analytical Accuracy of Principal Components

Element	5-day relative standard deviation (%)	Relative standard deviation of 2.5h (%)
Li	0.9	0.7
Co	0.8	0.8
Ni	0.7	0.7
Mn	0.5	0.7
molar ratio of Li/Co + Ni + Mn	0.9	0.3

Table 4 Quantitative Results of Major Components

Element	Wavelength (nm)	Detection limit (mg/L)	Detection limit In Solid (%)	Method Blank (mg/L)	Concentration (mg/L)	Concentration in Solid (%)	Theoretical value (%)	Recovery to the theoretical value (%)
Li	670.784	0.02	0.02	N.D.	7.2	7.2	7.2	100
Co	228.616	0.02	0.02	N.D.	12.2	12.2	12.3	99
Ni	231.604	0.02	0.04	N.D.	24.6	24.6	24.4	101
Mn	257.610	0.002	0.0009	N.D.	23.0	23.0	22.8	101

N.D.: Below detection limit
Detection limit: 3 × σ (standard deviation of STD1) × slope of calibration curve
Solid determination result = (Undoped sample – Method blank) × dilution ratio

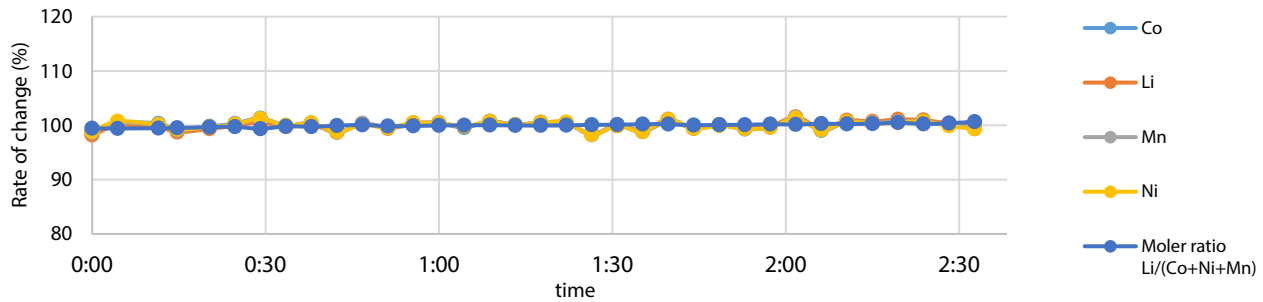


Fig. 4 Long-Term Stability of Main Components

■ Standard Sample for Elemental Impurity Analysis

Calibration curve samples were prepared by mixing commercially available standard solutions and adding nitric and hydrochloric acid at 1 % each. The concentrations of the measured elements in each calibration curve sample are shown in Table 6.

LIBs cathode materials are known to contain a large amount of Li as one of the major components. Since ionization interference is likely to occur when an alkali element such as Li is contained in large amounts, Li was added to the standard solutions at 70 mg/L to match the matrix level of the standard solutions and the sample solutions.

Table 6 Standard Sample Concentrations for Elemental Impurity Analysis

Element	STD1 (mg/L)	STD2 (mg/L)	STD3 (mg/L)	STD4 (mg/L)	STD5 (mg/L)	STD6 (mg/L)	STD7 (mg/L)
Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mo, Na, P, Pb, Sb, Si, Ti, V, Zn	0	0.1	0.2	0.5			
S	0				0.2	0.5	1
Li	70						
Nitric acid	1 v/v%						
Hydrochloric acid	1 v/v%						

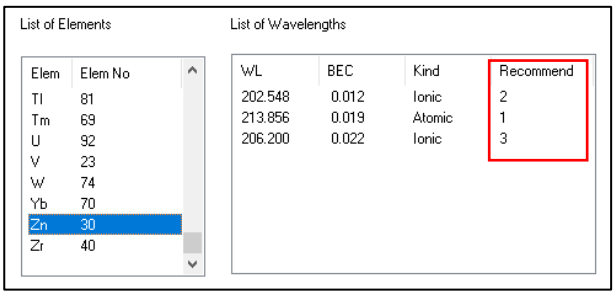


Fig. 5 Element and Wavelength Registration Screen

■ Analysis Wavelength of Elemental Impurity Analysis

The wavelength recommended by the ICPEsolution software as the analysis wavelength was chosen. ICPEsolution enables users to identify recommended wavelengths that have a low background equivalent concentration (BEC) and are generally less susceptible to interference from the wavelengths registered for each element (Fig. 5). The sample for elemental impurity analysis was analyzed with the calibration standards shown in Table 6.

Since the cathode materials contain a large amount of Li, Co, Ni, and Mn, spectroscopic interference from these major elements may occur during the analysis of elemental impurities. Therefore, it is important to select the optimal wavelength, one that is unaffected by spectral interference.

The 202.548 nm and 213.856 nm wavelengths of Zn have high sensitivity with low BEC (Fig. 5), but the peaks of Ni and Co overlap at 202.548 nm, and the peaks of Ni overlap at 213.856 nm (Fig. 6).

As shown in Fig. 5, ICPEsolution allows users to check which element peaks are likely to overlap using the "Peak Search" function. In addition, the "All-wavelength Data Acquisition" function allows data readout after measurement. Even if the major components are unknown, qualitative analysis of all elements can be added after the measurement, and it is easy to determine which elements are contained in large amounts. Using this function, users can confirm and quantify the profile of a wavelength that has not been registered without needing to re-measure. In this study, 206.200 nm, which is free from interference, was used for quantitative analysis of Zn (Fig. 7).

S has relatively low BEC at 180.731 nm and 182.037 nm, but Mn interferes with both. At 182.625 nm, there is slight B interference B, but since it was confirmed that the concentration of B in the sample was below the detection limit, 182.625 nm was used.

If the sample contains a large amount of B, it is better to perform inter-element correction at 180.731 nm, where the Mn interference is relatively small. With ICPEsolution, the user can easily perform inter-element correction by simply selecting the elements and wavelengths to be used for the operation. Care must be taken in cases where the correction amount is much larger than the quantitative value of S since an error is likely to occur (Fig. 8).

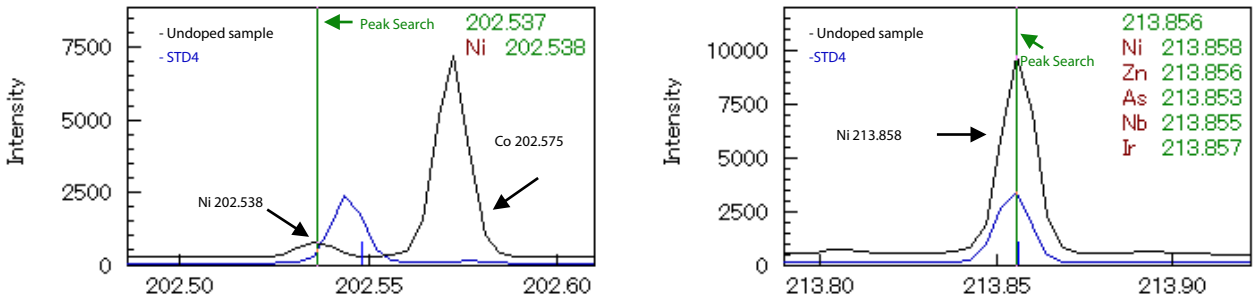


Fig. 6 Profile of Zn202.548 nm (Left) and 213.856 nm (Right)

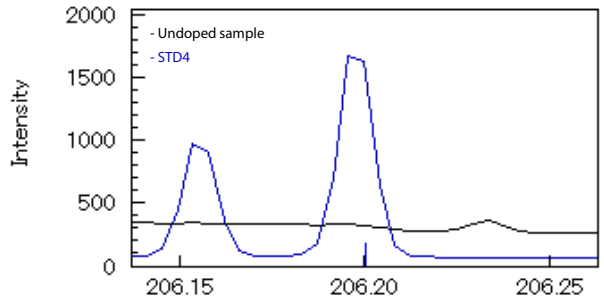
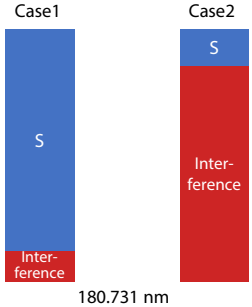


Fig. 7 Profile of Zn206.200 nm



In case 1, the amount of interference of Mn with S is small, but in case 2, the amount of interference, that is, the amount of correction, is large, so errors are likely to occur.

Fig. 8 Interelement Correction

■ Quantitative Results of Elemental Impurities

A calibration curve was prepared using the sample shown in Table 6 to determine elemental impurities in the cathode material. The quantitative results and spike recovery test are shown in Table 7. Good recovery rates of 95 % to 106 % were obtained for all elements.

In addition, in China, one of the major producers of LIBs cathode materials, the upper limit of the content of some elemental impurities is specified in YS/T 798 -2012[1]. The detection limit in solids was determined to be sufficiently sensitive to confirm this.

■ Conclusion

In this Application News, the ICPE-9820 was used to analyze the major components and elemental impurities in LIBs cathode materials.

Analysis of the major components showed that the results were stable over long periods and showed little day-to-day variation.

Good results were obtained in the analysis of elemental impurities in spike recovery tests, and the validity of the analysis was confirmed. In addition, elements and wavelengths were added after the measurement, and it was possible to determine the appropriate analytical wavelength without re-measurement.

The ICPE-9820 offers both low running costs and stable measurements. In addition, convenient functions such as the acquisition of all wavelength data make it possible to efficiently analyze even samples with high spectral interference. Therefore, the ICPE-9820 is the ideal instrument for elemental analysis of LIBs cathode materials.

Table 7 Quantitative Results of Elemental Impurities

Element	Wavelength (nm)	Detection limit (mg/L)	Detection limit in Solid (mg/kg)	YS/T 798-2012 reference value (mg/kg)	Method blank (mg/L)	Unspiked sample (mg/L)	Concentration in Solid (mg/kg)	Spiked concentration (mg/L)	Recovery rate (%)
Al	396.153	0.0009	0.9		N.D.	0.0854	85.4	0.2	99
B	182.640	0.002	2		N.D.	N.D.	N.D.	0.2	97
Ba	455.403	0.00002	0.02		N.D.	N.D.	N.D.	0.2	100
Ca	317.933	0.0004	0.4	300	0.0604	0.0342	N.D.	0.2	95
Cd	214.438	0.00007	0.07		N.D.	N.D.	N.D.	0.2	97
Cr	206.149	0.001	1		N.D.	N.D.	N.D.	0.2	99
Cu	324.754	0.0004	0.4	300	N.D.	N.D.	N.D.	0.2	103
Fe	259.940	0.003	3	300	N.D.	0.007	7.2	0.2	98
K	769.896	0.001	1		N.D.	N.D.	N.D.	0.2	106
Mg	285.213	0.0002	0.2	300	N.D.	0.0073	7.3	0.2	97
Mo	202.030	0.0006	0.6		N.D.	0.0139	13.9	0.2	100
Na	589.592	0.002	2	300	N.D.	0.033	33	0.2	105
P	178.287	0.01	10		N.D.	0.03	30	0.2	95
Pb	220.353	0.003	3		N.D.	0.100	100	0.2	96
S	182.625	0.09	90	2500	N.D.	0.49	490	1	96
Sb	206.833	0.01	10		N.D.	0.019	19	0.2	98
Si	212.412	0.001	1	300	N.D.	N.D.	N.D.	0.2	100
Ti	337.280	0.0002	0.2		N.D.	N.D.	N.D.	0.2	99
V	292.402	0.0009	0.9		0.0069	N.D.	N.D.	0.2	99
Zn	206.200	0.0004	0.4	300	N.D.	0.0016	1.6	0.2	96

Detection limit: 3 × σ (standard deviation of STD1) × slope of calibration curve
N.D.: Below detection limit
Solid determination result = (Undoped sample – Method blank) × dilution ratio
Recovery (%) = (Spiked sample – unspiked sample)/spiked concentration × 100

< References >

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.

< Related Applications >

1. Analysis of Elemental Impurities in Anode Materials for Lithium-Ion Secondary Batteries Using the ICPE 9820
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