

Determination of Elements in Ternary Material Nickel-Cobalt-Manganese Hydride

Determination of 25 elements in materials for lithium battery cathodes using ICP-OES



Author

Feng Wenkun, Ni Yingping
Agilent Technologies
(China) Co., Ltd.

Introduction

In recent years, the production and sales of new electric vehicles in China has continued to grow, which has boosted the demand for lithium-ion batteries and cathode materials. The cathode material used for lithium-ion batteries are lithium oxides. Most research focuses on the use of lithium cobaltate, lithium manganate, lithium iron phosphate and lithium nickel cobalt manganese oxide (a ternary compound consisting of three metal elements) for cathode materials. Since the introduction of the new energy vehicle mandate policy in 2017, the Chinese government has made continuous changes to the consumer subsidy program. Because of this, cathode materials that affect the energy density of lithium-ion batteries have attracted much attention. Among them, ternary materials (especially high-nickel ternary materials) have become the choice for cathode materials for new electric vehicle power batteries, which are in line with China's current requirements and account for the large growth in the cathode material market size.

There is a Chinese standard (YS/T 798-2012) that specifies the major elements and impurity elements that need to be measured in ternary material nickel-cobalt-manganese oxide (7), but it does not specify testing methods. In the absence of regulated methods, flame atomic absorption spectrometry (FAAS) and chemical titration are used. However, FAAS has many limitations which include:

1. The possible presence of easily ionized elements such as Na and K can cause chemical interferences at elevated levels, producing poor results.
2. A narrow linear range which may require multiple dilutions to allow the successful analysis of concentrated samples.
3. Lower sensitivity, due to low flame temperature.

Due to a limitation in sensitivity, the chemical titration method is generally only used to measure the major elements. The method's lack of precision demands multiple measurements, which greatly increases the labor requirements to complete analysis.

In this study, the Agilent 5110 Vertical Dual View (VDV) Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-OES) was used to establish a rapid analysis method for determining impurities and major elements in lithium nickel cobalt manganese oxide. ICP-OES offers superior performance, significant analysis efficiency improvements and reduced cost of analysis, compared to FAAS.

The Agilent 5110 VDV measures the trace elemental impurities using an axial view of the plasma. Major elements are measured using a radial view. This dual view method extends the upper measurement range, and reduces interferences for elements like Na and K, while allowing the determination of trace elements.

This study focuses on the quantification of Al, As, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mo, Na, P, Pb, S, Si, Sr, Ti, Zn and Zr in lithium nickel cobalt manganese oxide, along with the four main elements Ni, Co, Mn and Li.

Experimental

Instrumentation

All measurements were performed using the Agilent 5110 VDV ICP-OES. The instrument features the vertically-oriented torch which is capable of handling a range of complex sample types such as high-salt and high-base samples. The Vista Chip II CCD detector provides a wide dynamic linear range for effective analysis of trace and major elements, eliminating additional sample dilutions, avoiding errors caused by large dilutions.

The sample introduction system consisted of a SeaSpray concentric glass nebulizer, double-pass glass cyclonic spray chamber and a standard 1.8mm ID injector torch. Instrument operating parameters are shown in Table 1.

Table 1. Agilent 5110 VDV ICP-OES operating parameters.

Parameter	Setting	
Elements	Al, As, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mo, Na, P, Pb, S, Si, Sr, Ti, Zn and Zr	Ni, Co, Mn, Li
Viewing mode	Axial	Radial
Viewing height (mm)	N/A	8
Read time (s)	10	3
Replicates	3	
Sample Uptake delay (s)	12	
Stabilization time (s)	8	
Fast pump (rpm)	60	
Pump speed (rpm)	12	
RF power (kW)	1.2	
Plasma flow rate (L/min)	12	
Aux flow rate (L/min)	1.0	
Nebulizer flow rate (L/min)	0.7	
Background correction	Fitted	
Sample tubing	White/White	
Waste tubing	Blue/Blue	

Preparation of samples

Two commercially available lithium nickel cobalt manganese oxide samples were purchased for analysis (Sample A and Sample B). The lithium nickel cobalt manganese oxide samples were digested according to the following steps:

1. 0.3 g of each solid sample was accurately weighed into the polytetrafluoroethylene digestion tank;
2. 2–3 mL of concentrated aqua regia (High-purity nitric acid and high-purity hydrochloric acid, Suzhou Jingrui Company) was slowly added and capped;
3. The solution was heated to 120 °C on a hot plate for 30 min until the solution was transparent;
4. After cooling, digests were made up to 30 mL with ultrapure water.

This solution was used to measure trace elemental impurities (Solution 1). An aliquot of the Solution 1 was taken and further diluted 1:1 with ultrapure water. This solution was used to analyze lithium, nickel, cobalt, and manganese (Solution 2). Each sample digest was prepared in duplicate for both solution 1 and solution 2, as well as duplicate digestion blanks.

Preparation of standards

The method of standard addition was used to give better accuracy in determining the trace elemental impurities. Due to the complex nature of the samples, these were difficult to matrix match and standard additions were used to minimize physical and chemical differences between standards and samples.

Calibration standards were prepared by standard addition using Agilent 10 mg/L multi- element standard solution-2A at 0.01, 0.05, 0.2, 0.5 and 1 mg/L by spiking with aliquots of sample Solution 1.

To prepare S and Si standard solutions, a Agilent 10 mg/L multi-element standard solution was used, with standard additions at 0.01, 0.05, 0.2, 0.5 and 1 mg/L by spiking aliquots of sample Solution 1.

To prepare standards for nickel, cobalt, and manganese oxide, Agilent single element 1000 mg/L standard solutions for Ni, Co and Mn were used. Standard solutions at concentrations: 50, 100, 200, 500, and 900 mg/L were prepared in 1% nitric acid.

Agilent single element 1000 mg/L standard solution for Li was used to prepare standard solutions for lithium at 20, 50, 100, 200, and 400 mg/L in 1% nitric acid.

Results and Discussion

Calibration linearity

When analyzing trace elemental impurities in lithium nickel cobalt manganese oxide, the standard addition method was used for quantitative analysis. Linear calibrations were obtained for all 21 elemental impurities with correlation coefficients greater than 0.9995. Figure 1 shows the peak shapes and intensities of As, P and Si, which are traditionally more difficult to analyze with ICP-OES. The spectra show that excellent sensitivity was achieved by the Agilent 5110 ICP-OES for these elements.

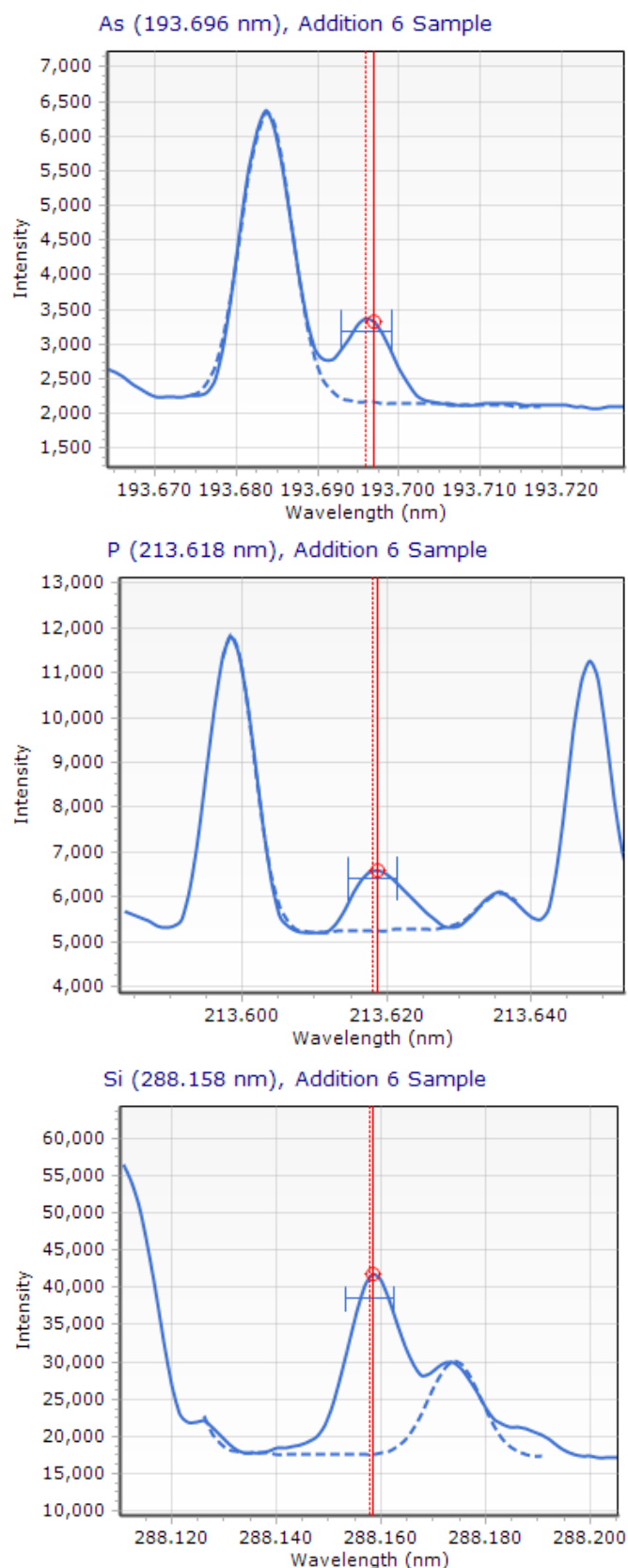


Figure 1. Peak shapes and intensities for the As, P and Si emission lines.

The corresponding calibration curves for As, P and Si are displayed in Figure 2.

When analyzing the major elements in lithium nickel cobalt manganese oxide, quantitative analysis was carried out using a standard curve method. The results of the standard curve method show linear calibrations and correlation coefficients greater than 0.9995 for Ni, Co, Mn and Li (Figure 3).

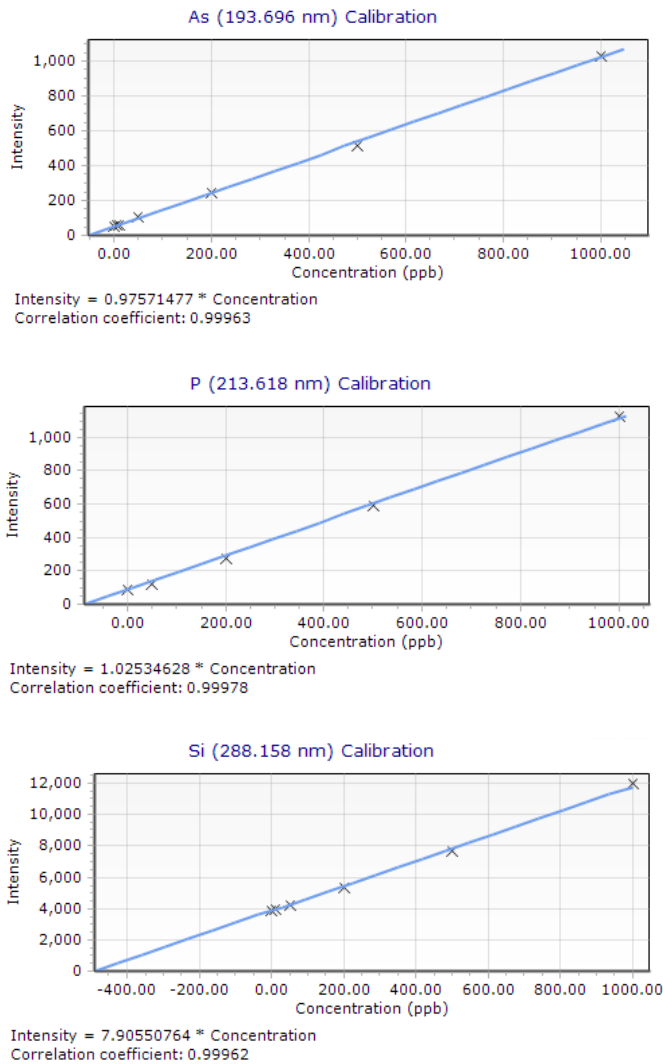


Figure 2. As, P, Si standard curves (0, 0.01, 0.05, 0.2, 0.5, and 1 mg/L) by standard addition.

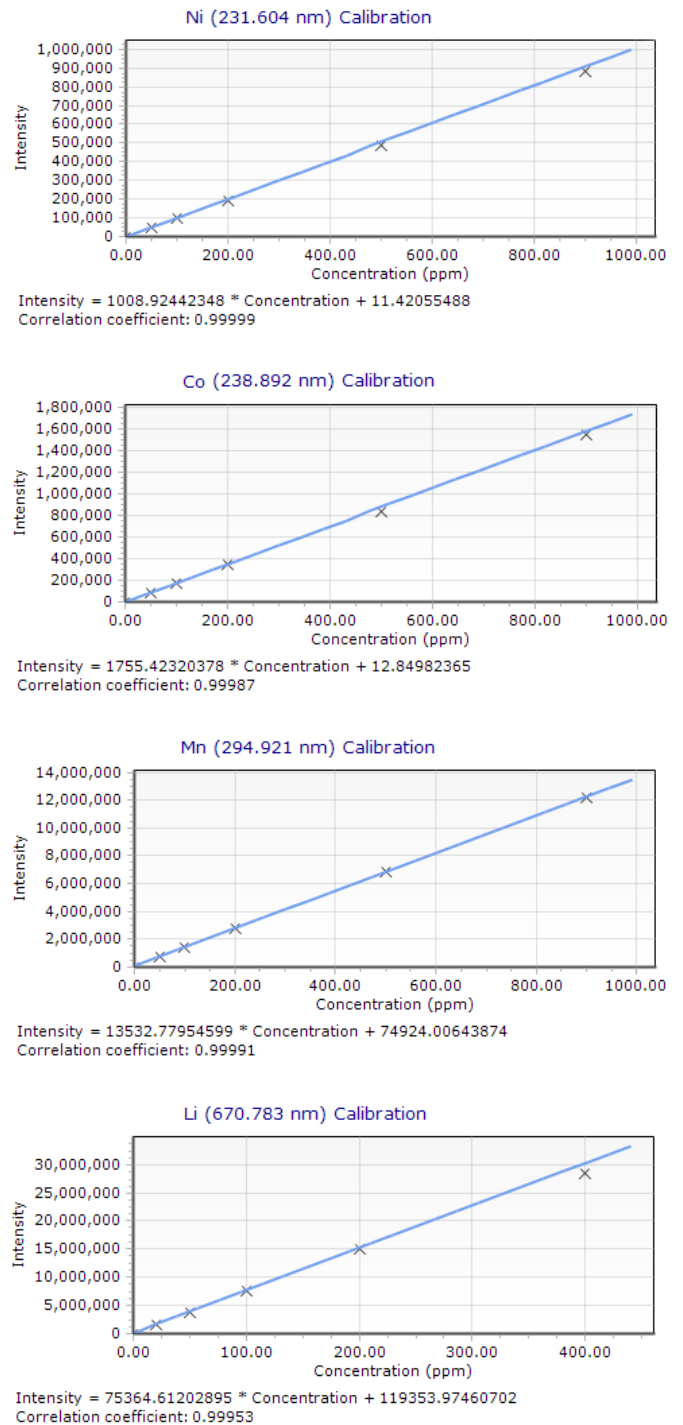


Figure 3. Calibration curves for (Ni, Co, Mn 50, 100, 200, 500, 900 mg/L; Li 20, 50, 100, 200, 400 mg/L).

Method detection limits

The Method Detection Limits (MDLs) were based on three sigma of eleven replicate measurements of the preparation blank solutions (a digested blank, taken through the digestion process) during an analytical run. The MDLs for the elemental impurities and major elements in are shown in Table 2 and Table 3, respectively.

Table 2. Method detection limits for elemental impurities in lithium nickel cobalt manganese oxide samples.

Element and wavelength	MDL (mg/kg)	Element and wavelength	MDL (mg/kg)
Al 396.152	0.054	Mo 204.598	0.048
As 193.696	1.345	Na 589.592	0.918
Ba 493.408	0.016	P 213.618	0.553
Be 313.107	0.015	Pb 220.353	0.194
Ca 396.847	0.097	S 182.562	0.443
Cd 214.439	0.026	Si 288.158	0.381
Cr 206.158	0.199	Sr 407.771	0.024
Cu 324.754	0.032	Ti 334.941	0.106
Fe 259.940	0.21	Zn 206.200	0.193
K 766.491	0.019	Zr 343.823	0.037
Mg 279.553	0.048		

Table 3. Method Detection Limits for major elements (Ni, Co, Mn and Li) in lithium nickel cobalt manganese oxide samples.

Element and wavelength	MDL (mg/kg)	Element and wavelength	MDL (mg/kg)
Ni 231.604	0.893	Mn 294.921	0.143
Co 238.892	0.569	Li 670.783	1.161

Sample analysis and spike recovery

The lithium nickel cobalt manganese oxide samples A and B were analyzed, and spike recovery experiments carried out for the elemental impurities to validate the method. Considering that the concentration limit of most elements is less than 0.003%, the samples were spiked at a concentration of 100 µg/L. The results show that the recoveries of all elements were between 92% and 110% , except for As. The concentration of Na, S and Si in the samples was significantly higher than the spiked concentration of 100 µg/L and the recovery % could not be accurately determined, thus have been excluded from the results shown in Table 4. The results of the determination of the four major elements in samples A and B are shown in Table 5.

Table 4. Sample and spike recovery results for elemental impurities in Sample A and Sample B.

	Al 396.152	As 193.696	Ba 493.408	Be 313.107	Ca 396.847	Cd 214.439	Cr 206.158
Sample A µg /L	172.7	10.1	2.4	ND	140.6	16.6	56.2
Sample A +100 µg /L	265.3	122.5	109.8	106.5	246.9	119.6	155.8
Recovery %	93	112	107	107	106	103	100
	Cu 324.754	Fe 259.940	K 766.491	Mg 279.553	Mo 204.598	Na 589.592	P 213.618
Sample B µg /L	169.8	15.7	2.5	ND	136.9	16.3	64.7
Sample B +100 µg /L	274.1	109.3	110.5	106.8	246.8	120.3	163.6
Recovery %	104	94	108	107	110	104	99
Sample A µg /L	ND	113.8	5.0	59.1	3.5	3802.9	80.1
Sample A +100 µg /L	106.3	210.6	107.8	166.0	103.6	/	179.6
Recovery %	106	97	103	107	100	/	99
Sample B µg /L	ND	115.5	4.8	58.7	2.4	3752.1	75.8
Sample B +100 µg /L	105.2	209.7	108.2	166.1	99.3	/	174.8
Recovery %	105	94	103	107	97	/	100
	Pb 220.353	S 182.562	Si 288.158	Sr 407.771	Ti 334.941	Zn 206.200	Zr 343.823
Sample A µg /L	271.4	1024.9	424.4	10.7	338.9	19.7	5.1
Sample A +100 µg /L	364.3	/	/	119.3	441.3	120.2	103.8
Recovery %	93	/	/	109	102	101	99
Sample B µg /L	264.7	980.1	436.5	10.7	340.3	26.4	3.1
Sample B +100 µg /L	363.3	/	/	120.2	441.6	122.0	102.2
Recovery %	92	/	/	109	101	96	99

Table 5. Results for major elements in Sample A and Sample B.

Element	Sample A (mg/kg)	Sample B (mg/kg)
Ni 231.604	324958.34	317295.43
Co 238.892	103767.16	104758.85
Mn 294.921	98227.42	97940.37
Li 670.783	66795.26	66807.71

Long-term stability

The long-term stability of the Agilent 5110 VDV ICP-OES was investigated by analyzing a spiked sample B solution of lithium nickel-cobalt manganese oxide. Spike solutions of 100 µg/L were added to determine long-term stability for elemental impurities. Sample B solution was used to determine the long-term stability for the major elements. The two groups of samples were tested continuously for 2.5 h and the results are shown in Table 6. The relative standard deviation (RSD) of the elemental impurities was less than 3.5%, and the RSD of the major elements was less than 1%. This demonstrates the 5110's excellent stability and reliability over the duration of the analytical run.

Table 6. Long-term stability results of major elements and impurities in lithium nickel cobalt manganese oxide samples.

Element	RSD (%)	Element	RSD (%)	Element	RSD (%)	Element	RSD (%)
Al	0.7	Cu	1	Pb	1.7	Ni	0.3
As	3.4	Fe	3.4	Sr	0.6	Co	0.8
Ba	0.5	K	0.5	Ti	0.8	Mn	0.5
Be	0.7	Mg	0.9	Zn	2.8	Li	0.4
Ca	0.6	Mo	1.8	Zr	1.2		
Cd	0.9	Na	0.7				
Cr	3.1	P	3.4				

Conclusions

The Agilent 5110 Vertical Dual View (VDV) ICP-OES demonstrated excellent performance for the analysis of cathode material, lithium nickel cobalt manganese oxide, in lithium batteries. With its vertically oriented torch design, the 5110 was capable of handling high lithium and high-salt samples.

Recoveries of 20 of the 25 elements measured were within $\pm 10\%$ of the actual concentrations. Na, S and Si in the samples was significantly higher than the spiked concentration of 0.10 mg/L and the recovery could not be accurately determined.

The 5110 delivered excellent linear dynamic range, allowing the measurement of trace elemental impurities and major elements in lithium nickel cobalt manganese oxide meaning no additional dilutions were required, avoiding errors introduced by multiple dilutions.

References

1. Chinese method YS/T 798-2012 lithium nickel cobalt manganese oxide

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This information is subject to change without notice.