Application Note
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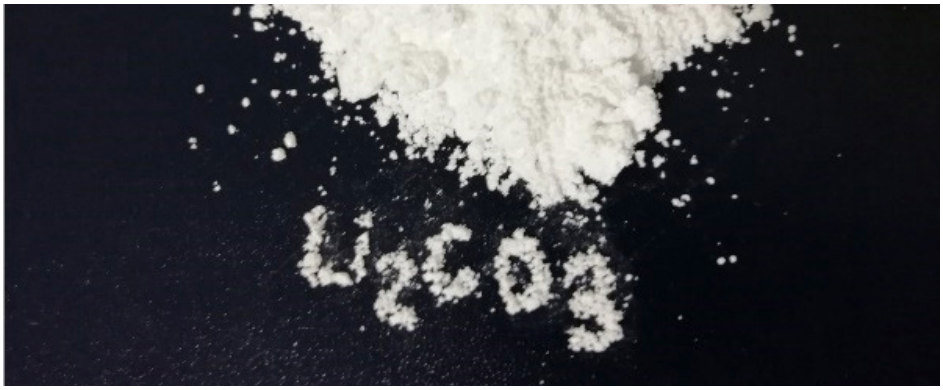
Determination of 14 Impurity Elements in Lithium Carbonate Using ICP-OES

Routine quality control of raw materials used to produce cathode material for lithium ion batteries



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Introduction

As part of their efforts to combat climate change, many countries are reducing the amount of energy that is generated from burning fossil fuels by switching to renewable energy sources. However, to meet the energy demands of the transport, heating, or industrial sectors from renewables, efficient and cost-effective energy storage technologies are needed. Lithium (Li)-ion batteries are widely used in consumer electronic devices due to their large capacity, high voltage, light weight, and lack of memory effects. These properties also make them attractive for use in electric or hybrid vehicles. Among the components of a Li-ion battery (cathode, anode, separator, and electrolyte), the materials used for the cathode account for more than 40% of the total cost of the battery. Lithium carbonate (Li_2CO_3) is a key raw material that is used to prepare cathode materials and the quality of the material determines the price. Also, any impurities present in the raw materials

used to make the battery can affect its performance and lifespan. Therefore, impurity analysis of battery-materials is vital for suppliers of the raw materials, battery manufacturers, and emerging industries such as the electric vehicle power battery sector (*1–3*).

The elemental analysis of battery-grade Li_2CO_3 is often based on the methods outlined in International Electrotechnical Commission (IEC) 62321 standard and in Chinese standard GB/T 11064.16-2013 (*4, 5*). Both standards use an external calibration ICP-OES method for the analysis. The presence of many lithium ions in the plasma from Li_2CO_3 can affect the analysis of easily ionized elements (EIEs) such as Na and K by ICP-OES, leading to false-positive results. To minimize or eliminate the EIE interferences, the plasma of the ICP-OES can be viewed radially. But radial view measurements typically lack the sensitivity required for the analysis of trace elements in battery-grade Li_2CO_3. Also, the ultraviolet visible (UV-Vis) spectrophotometric method adopted for the measurement of silicon (Si) in GB/T 11064.16-2013 lacks accuracy and is complicated. Being able to determine all target elements, including Si, in a single analysis by ICP-OES would simplify the analysis, improve the quality of the data, and increase productivity.

In this study, the Agilent 5110 Vertical Dual View (VDV) ICP-OES was used for the measurement of Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si, and Zn in Li_2CO_3 using the method of standard addition (MSA). MSA was used to minimize the differences between the standards and samples. It also allows Na and K to be measured axially, ensuring that all elements are measured in a single plasma view mode.

Experimental

Instrumentation

The Agilent 5110 VDV ICP-OES with a vertically orientated torch was used in this study. The sample introduction system consisted of a SeaSpray concentric glass nebulizer, double-pass glass cyclonic spray chamber, and an Easy-fit demountable VDV 1.8 mm inner diameter (id) injector torch.

The 5110 ICP-OES uses a solid-state radio frequency (SSRF) generator operating at 27 MHz to deliver a plasma with the stability and robustness necessary for the analysis of high matrix samples such as Li_2CO_3. The fast processing speed of the VistaChip III CCD detector, up to 1 MHz pixel processing speed, reads the full wavelength range in a single exposure. With such fast analysis speeds, the argon gas consumption per sample is typically lower than other ICP-OES instruments. The detector also provides a wide dynamic linear range for effective analysis of trace and major elements in the same run. The wide analytical range eliminates the need for extra sample dilutions or multiple readings of the same sample, increasing sample throughput. Also, avoiding extra sample dilutions prevents introducing potential errors caused by large dilutions or reducing the analyte signal below its detection limit. The 5110 features a cooled cone interface (CCI) that improves the reliability of the results by reducing the formation of EIE interferences. Instrument operating parameters are shown in Table 1.

Table 1. Operating parameters of the 5110 VDV ICP-OES.

Parameter	Setting
Viewing Mode	Axial
Read Time (s)	10
Replicates	3
Stabilization Time (s)	8
Fast Pump (rpm)	60
Pump Speed (rpm)	12
Power (kW)	1.2
Plasma Gas Flow (L/min)	12
Auxiliary Gas Flow (L/min)	1.0
Nebulizer Gas Flow (L/min)	0.7

Background correction

The ICP Expert instrument control software includes easy-to-use background correction techniques including Fitted Background Correction (FBC). FBC accurately corrects background structures without user intervention or method development. An example of automatic background fitting using FBC from this study is shown for Pb 220.353 in Figure 1. FBC provides accurate correction of the background structure that can arise from other emission lines in the sample, allowing more accurate measurements (*6*).

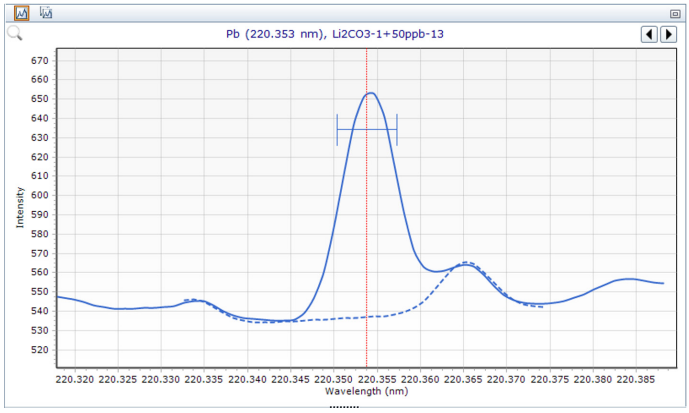


Figure 1. Automatic FBC has accurately modeled the Nb 220.363 interfering peak on Pb 220.353 nm.

Reagents, standard solutions, and samples

High purity nitric acid was bought from Suzhou Jingrui Chemical Company (China). Calibration standards were prepared using Agilent standards, including a 10 mg/L multi-element standard solution 2A and a 10 mg/L multi-element standard solution-4. A commercial Li_2CO_3 sample was bought for the study.

Sample preparation

To prepare the Li_2CO_3 sample for analysis, 0.3 g of solid sample was weighed into a PTFE digestion tube. 2–3 mL of concentrated HNO_3 was added slowly. (SiO_2 is removed from Li_2CO_3 during the extraction process, so no HF was added during the digestion of Li_2CO_3). The tube was covered and heated on a hotplate for 120 minutes at 120 °C until the solution was clear and transparent. After cooling, the solution was made up to 30 mL with ultrapure water (Millipore Milli-Q). For the long-term stability test, the sample was spiked at 50 µg /L.

At the same time as preparing the sample, another aliquot of the Li_2CO_3 sample was prepared to be used as a matrix solution for the MSA calibration. A digestion blank was also prepared by digesting 2–3 mL HNO_3 and making up to 30 mL.

The sample, spiked sample, and digestion blank were prepared in duplicate.

Preparation of MSA calibration standards

To prepare the multi-element calibration standards, 100 µL of the Agilent multi-element standard solution-2A was diluted to 5 mL with the matrix solution to a concentration of 0.2 mg/L. 50, 100, 200, 500, and 1000 µL of this intermediate standard solution were then diluted to 2 mL with the matrix solution. This method produced a series of standards solutions at 0.005, 0.01, 0.02, 0.05, and 0.1 mg/L.

A series of standard solutions of S and Si were prepared at 0.01, 0.02, 0.05, and 0.1 mg/L. An intermediate standard solution for S and Si was prepared by diluting 100 µL of multi-element standard solution-4 to 5 mL with the matrix solution. 100, 200, 500, and 1000 µL of the 0.2 mg/L intermediate standard were diluted to 2 mL with the matrix solution.

Results and discussion

Calibration and linearity

Using MSA, linear calibration curves were obtained for all 14 elements. The calibration correlation coefficients were greater than 0.9995 in all cases. Figure 2 shows the calibration curves for seven representative elements including Na, K, Ca, Cd, Fe, Mg, and Si.

Method detection limits

The MDLs shown in Table 2 are based on three sigma measurements of 11 samples of the matrix solution that were measured continuously. All MDLs were well below 1.0 mg/kg, allowing impurities to be detected and monitored at low levels in battery-grade Li_2CO_3.

Table 2. Method detection limits for 14 elements.

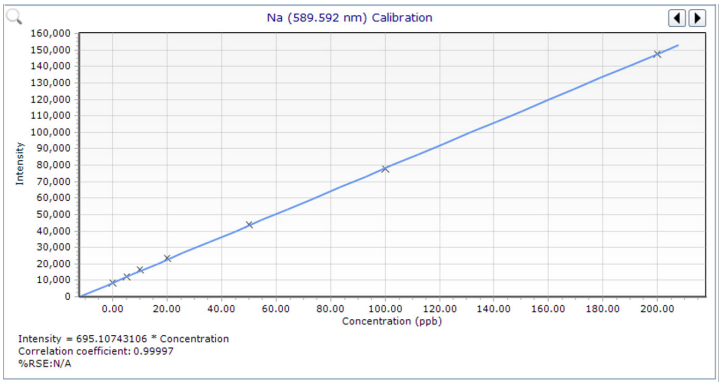
Element and Wavelength (nm)	MDL in Sample (µg /L)	Element and Wavelength (nm)	MDL in Sample (µg /L)
Al 396.152	1.1	Mn 257.610	0.03
Ca 422.673	0.080	Na 589.592	0.08
Cd 226.502	0.16	Ni 216.555	1.9
Cu 327.395	0.29	Pb 220.353	8.2
Fe 238.204	0.42	S 181.972	6.0
K 766.491	0.24	Si 251.611	5.6
Mg 279.553	0.030	Zn 213.857	0.65

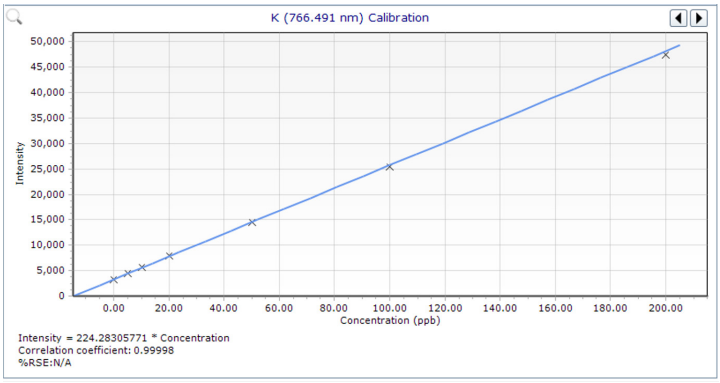
Sample analysis and spike recovery

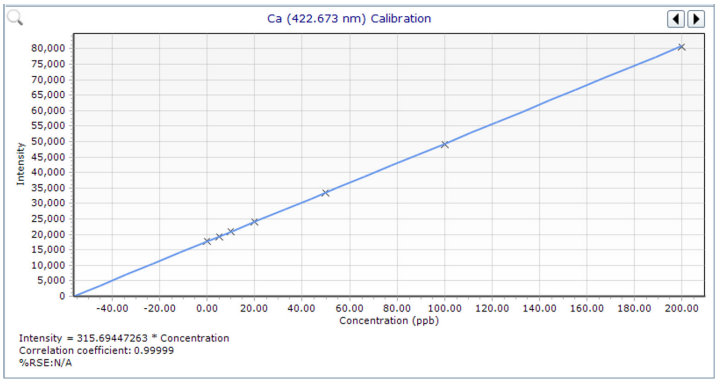
The digest of the commercial Li_2CO_3 sample was analyzed using the 5110 ICP-OES method and the results are given in Table 3. To test the accuracy of the measurements, a spike recovery test was carried out at a concentration of 50 µg/L. The recoveries of all elements were between 95 and 102% (Table 3), confirming the suitability of the method for the determination of impurities in Li_2CO_3 at trace levels.

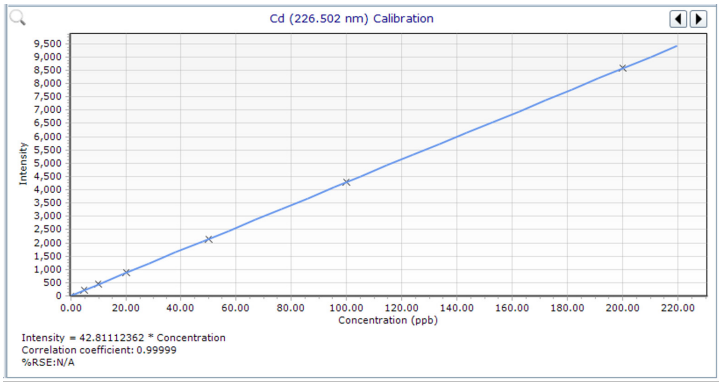
Table 3. Sample and spike recovery results for elemental impurities in battery-grade Li_2CO_3.

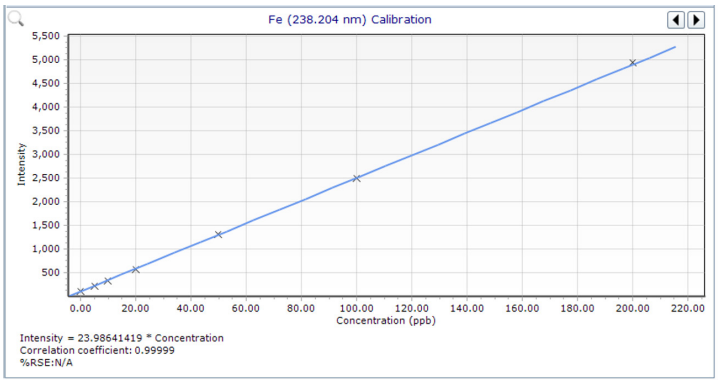
Element and Wavelength (nm)	Measured Concentration in Sample (µg/L)	Sample + Spike at 50 (µg /L)	Recovery (%)
Al 396.152	1.3	52	100
Ca 422.673	19	68	99
Cd 226.502	<MDL	50.5	101
Cu 327.395	0.50	52	102
Fe 238.204	1.8	51	99
K 766.491	13	63	100
Mg 279.553	0.60	51	100
Mn 257.610	0.10	50	100
Na 589.592	11	60	98
Ni 216.555	<MDL	52.1	104
Pb 220.353	<MDL	51.2	102
S 181.972	30	78	96
Si 251.611	7.1	56	98
Zn 213.857	1.4	52	100

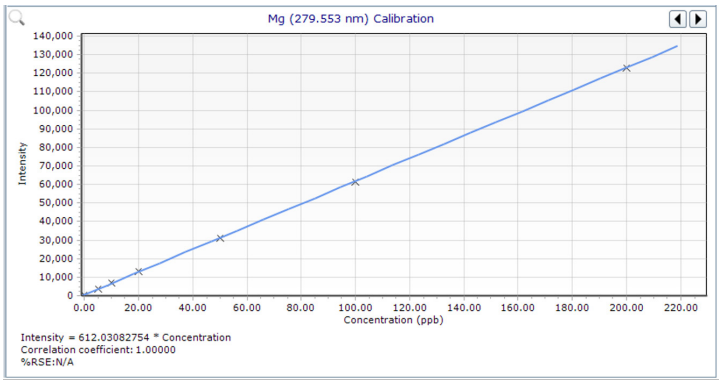












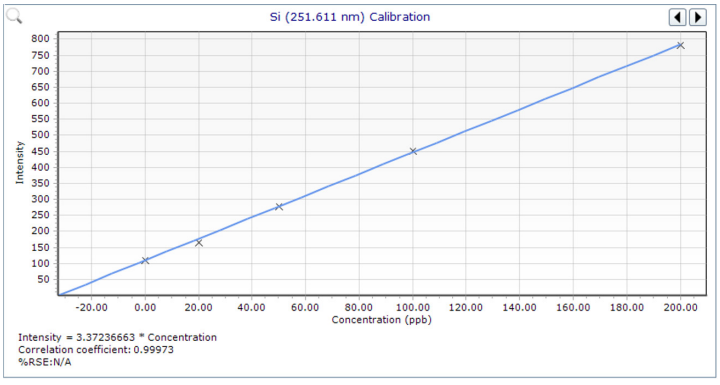


Figure 2. MSA calibration curves for Na, K, Ca, Cd, Fe, Mg, and Si.

Long-term stability

The long-term stability of the 5110 VDV ICP-OES was tested by continuously analyzing a sample solution of Li_2CO_3 spiked at 50 µg/L for 2.5 h. The relative standard deviation (RSD) of all elements was less than 2%, as shown in Table 4. The excellent precision demonstrates the stability, reliability, and robustness of the 5110 ICP-OES over the duration of the analytical run.

Table 4. Long-term stability results for 14 elements measured in Li_2CO_3 over 2.5 h.

Element and Wavelength (nm)	RSD (%)	Element and Wavelength (nm)	RSD (%)
Al 396.152	1.2	Mn 257.610	1.1
Ca 422.673	0.7	Na 589.592	0.8
Cd 226.502	1.2	Ni 216.555	1.9
Cu 327.395	0.6	Pb 220.353	1.7
Fe 238.204	1.2	S 181.972	1.9
K 766.491	0.6	Si 251.611	1.8
Mg 279.553	1.3	Zn 213.857	1.5

Conclusion

The Agilent 5110 VDV ICP-OES was used to quantify 14 impurity elements in battery-grade lithium carbonate—a raw material that is used in to produce the cathode of a Li-ion battery. Silicon was included in the ICP-OES method, avoiding the need to use a separate measurement technique such as UV-Vis. The fast processing speed of the Vista Chip III detector enabled all data to be collected in 60 seconds, boosting productivity, and saving on argon gas consumption and energy costs.

Recoveries of all 14 elements spiked at 50 µg/L into the Li_2CO_3 sample digest were within ±10% of the spiked concentrations. And the RSD of the 2.5 h stability test results was less than 2%. These results demonstrate the accuracy, stability, and reliability of the method and its suitability for the large-scale, routine QC of raw materials used in the production of Li-ion batteries.

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