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Determination of Elemental Impurities in Silicon-Carbon Anode Materials for Lithium-Ion Batteries by ICP-OES

Accurate, robust measurement of 25 elements using the Agilent 5800 ICP-OES

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Introduction

The global market for lithium-ion batteries (LIBs) is projected to grow from around US $44.5 billion in 2022 to US $135.1 billion by 2031 (*1*). Demand for LIBs is being driven mainly by the electric vehicle (EV) sector and by the need for large-scale energy storage systems for electricity generated from renewable sources. The anode is an essential component of a LIB, as it stores and releases Li ions during the charge/discharge cycle. The quality of the anode is therefore crucial to the performance of the battery. Most LIBs currently use graphite-based anodes due to the availability of graphite, its excellent electronic conductivity properties, and low cost. However, the drawbacks of graphite-based anodes, particularly their low specific capacity, have led to extensive research into the development of alternative anode materials (*2, 3*). Silicon-carbon composites have stood out as a promising alternative material to graphite (*4*). The new class of anodes benefit from the high volumetric and specific capacity of the silicon, while the carbon matrix maintains the structural integrity and electrical stability of the material (*2*). Silicon-carbon anode materials are currently one of the main alternative-graphite anode materials that are available commercially (*5, 6*).

Since the electrochemical properties of LIBs are affected by anode dopant and coating elements, as well as contaminants, developers, manufacturers, and users of anode materials require robust quality control (QC) testing methods. The analytical methods need to be suitable for the analysis of many sample types, including samples of different purities. As China is a leading producer of anode materials, it has issued national standards GB/T 24533-2019 (7) and GB/T 38823-2020 (8) for graphite anode materials and silicon-carbon, respectively. Both recommended standard methods require the analysis of trace elements, such as iron, sodium, chromium, copper, nickel, aluminum, molybdenum, cobalt, and zinc using Inductively Coupled Plasma Emission Spectrometry (ICP-OES) following microwave digestion of the samples. The same methodology was applied in this study. An Agilent 5800 Vertical Dual View (VDV) ICP-OES was used to measure 25 elements in high purity graphite (99.99%) and silicon-carbon sample digests. The method was evaluated through sample spiking, before and after sample preparation, and long-term stability testing.

Experimental

Materials and standard solutions

High purity concentrated nitric acid (HNO_3) (69%) and hydrochloric acid (HCl) (30%) were bought from Merck Pty. Ltd, Australia. Commercially available high purity graphite (99.99%) and a mixture of the graphite with a 99% silicon powder (9:1 wt) were used to represent graphite-based and silicon-carbon LIB anode materials, respectively. Calibration standards were prepared from Agilent 10 mg/L multi-elemental standard 2A (Al, As, Ba, Be Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn) and Agilent 1,000 mg/L single element standard solutions of Mo, Sb, Ti, and Zr. Internal standard (IS) solutions were prepared from Agilent single element standard solutions of Rb and Y at 10,000 mg/L.

Sample preparation

The microwave digestion method outlined in GB/T 24533-2019 (7) and GB/T 38823-2020 (8) was used to prepare the samples. About 0.2, 1, and 1 g of 99% silicon, 99.99% graphite, and silicon-carbon (graphite:silicon = 9 to 1 wt) samples, respectively, were accurately weighed to ± 0.0001 g. The samples were added to a dry clean microwave digestion tube. Each sample was thoroughly mixed in 14.4 mL aqua regia (AR) (11.4 mL HCl and 3 mL HNO_3 at 3 to 1 molar ratio). Blank samples and the sample spiked solutions were prepared using the same procedure and all solutions were prepared in triplicate. The graphite samples were spiked at 0.025, 0.05, and 0.1 mg/L before microwave digestion. The silicon-carbon sample digests were diluted 10 times and were spiked after microwave digestion.

The samples were digested using a Mars 6 Microwave Digestion System (CEM Corporation) at 200 °C, holding for 30 min. After digestion, each solution was made up to 50 mL using ultrapure water (Milli-Q), producing a 28.8% (v/v) AR sample matrix solution. The graphite, silicon, and silicon-carbon samples were then filtered through a 0.45 µm PTFE disc filter to remove undissolved carbon particles. Before ICP-OES analysis, each replicate of the digested silicon-carbon sample was diluted 10 times with 28.8% AR and spiked at 0.025 mg/L with all 25 elements. Ca, K, Mg, and Na were also spiked at 0.05 and 0.1 mg/L. For consistency, the unspiked sample solutions of silicon and silicon-carbon were also diluted 10 times before analysis.

Calibration standards and internal standards

A 10 mg/L stock solution containing Mo, Sb, Ti, and Zr was prepared by diluting each 1,000 mg/L single element standard solution in 5% HNO_3. To prepare calibration standard solutions in the analytical working range, the 10 mg/L four-element stock solution and the 10 mg/L Standard 2A were diluted to the desired concentrations using the 28.8% AR matrix solution. Most of the target analytes were calibrated using standards at 0, 0.005, 0.020, 0.050, 0.100, and 0.200 mg/L, while a 2.00 mg/L concentration standard was added for Al and Fe to cover the concentration ranges in the samples. Ca, K, and Na were calibrated using standard solutions at 0, 0.010, 0.050, 0.100, 0.200, and 0.500 mg/L.

For quality control purposes, a blank 28.8% AR solution was used as the continuing calibration blank (CCB). Two standard solutions (0.05 and 0.1 mg/L), which were prepared separately from the calibration standards, were used as continuing calibration verification (CCV and CCV1) solutions. The CCB and CCVs were analyzed every 10–12 samples. An IS solution containing 10 mg/L Y and 100 mg/L Rb was prepared in 28.8% AR.

Instrumentation

The elemental analysis of all samples was carried out using the 5800 VDV ICP-OES fitted with a SeaSpray glass concentric nebulizer, double-pass cyclonic spray chamber, and an Easy-fit fully demountable torch with 1.8 mm quartz injector. Sample introduction was performed using an Agilent SPS 4 autosampler. The instrument and method were controlled and optimized using Agilent ICP Expert software, which was also used to process the analytical data.

To provide the robustness and stability of the plasma over long analytical runs of complex LIB samples, the 5800 ICP-OES uses a vertical plasma, a solid-state radio frequency (SSRF) generator operating at 27 MHz, and a Cooled Cone Interface (CCI). The CCI deflects the plasma's cooler tail, avoiding interferences that form in the cooler region. So, when reading the vertical plasma in axial view mode, elements at trace concentration levels can be measured with minimal interfering effects.

The instrument operating conditions shown in Table 1 were optimized to take account of easily ionizable elements (EIEs), such as Ca, K, and Na. These elements have low ionization energies and are easily ionized in the plasma. If EIEs are present in a sample at a high enough concentration, the plasma electron density and the atomization-ionization equilibria are affected. These effects cause either an enhancement or suppression of the emission signals, leading to the reporting of either false high or false low element concentrations. Internal standards can be used to correct for these effects in the plasma. In this work, instrument operating conditions were evaluated and optimized based on calibration linearity and detection limits. Since the EIEs were present in the samples at low levels, axial viewing mode was used for all 25 elements.
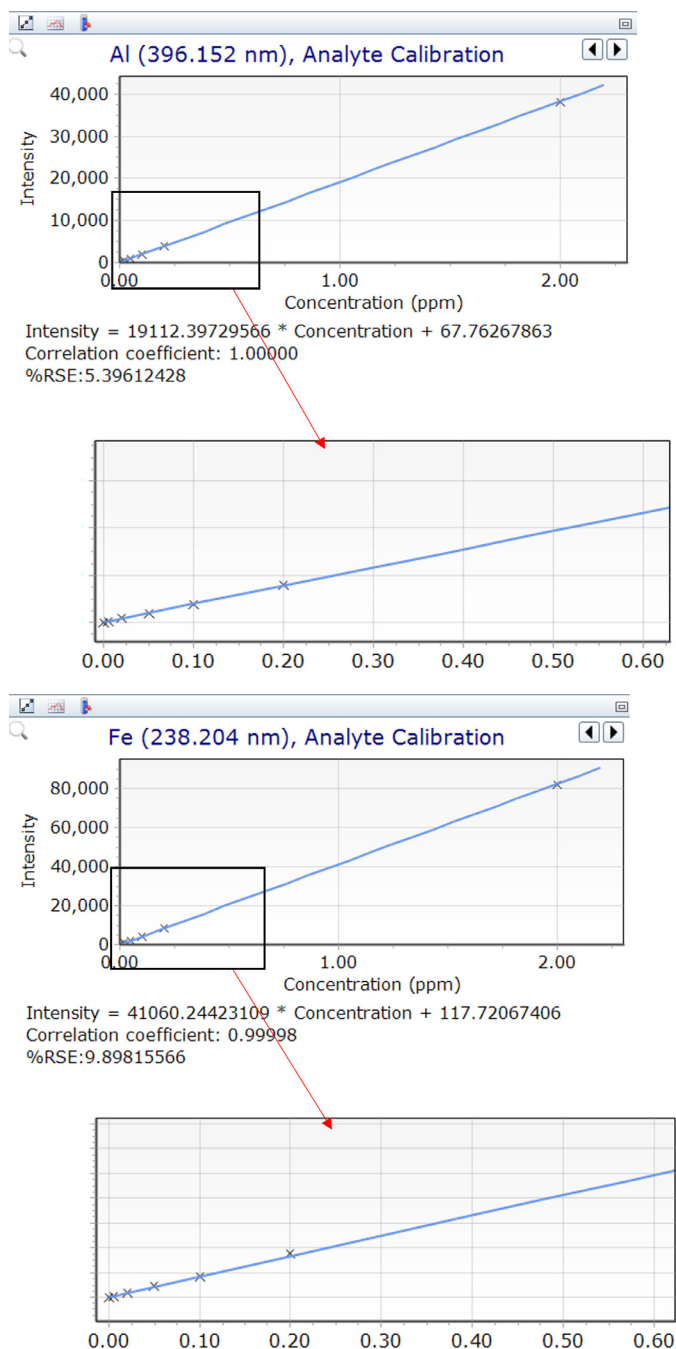
Table 1. Agilent 5800 VDV ICP-OES operating conditions.

Parameter	Setting
Viewing Mode	Axial
RF Power (kW)	1.2
Nebulizer Flow (L/min)	0.70
Plasma Flow (L/min)	12.0
Aux Flow (L/min)	1.0
Read Time (s)	15
Rinse Time (s)	30
Replicates	3
Stabilization Time (s)	15
Pump Speed (rpm)	12
Sample Uptake Delay (s)	25
Sample Pump Tubing	White/white
Internal Standard Pump Tubing	Orange/green
Waste Pump Tubing	Blue/blue

Results and discussion

Calibration linearity

The calibration correlation coefficients of the 25 elements at selected wavelengths are summarized in Table 2. Good linearity was achieved for all elements in their respective working ranges, as shown by R values close to 1. Representative calibration curves for Al 396.152 and Fe 238.204 nm are shown in Figure 1.

Al (396.152 nm), Analyte Calibration

Intensity = 19112.39729566 * Concentration + 67.76267863
Correlation coefficient: 1.00000
%RSE:5.39612428

Fe (238.204 nm), Analyte Calibration

Intensity = 41060.24423109 * Concentration + 117.72067406
Correlation coefficient: 0.99998
%RSE:9.89815566

Figure 1. Calibration curves of Al 396.152 nm and Fe 238.204 nm.

Table 2. Calibration range, correlation coefficient (R), background correction mode, and LOD and LOQ of graphite samples (calculated as 1 g sample in 50 mL solution) at selected wavelengths.

Element and Wavelength (nm)	Working Range mg/L	Correlation Coefficient	Background Correction Mode	LOD (mg/kg)	LOQ (mg/kg)
Al 396.152	0.005 – 2.00	1.0000	Fitted	0.056	0.19
As 188.980	0.005 – 0.200	0.9999	Fitted	0.095	0.32
Ba 455.403	0.005 – 0.200	1.0000	Fitted	0.0024	0.0080
Be 234.861	0.005 – 0.200	1.0000	Fitted	0.0020	0.0067
Ca 396.847	0.010 – 0.500	1.0000	Fitted	0.062	0.21
Cd 214.439	0.005 – 0.200	1.0000	Fitted	0.0061	0.020
Co 238.892	0.005 – 0.200	1.0000	Fitted	0.026	0.087
Cr 267.716	0.005 – 0.200	1.0000	Fitted	0.018	0.059
Cu 327.395	0.005 – 0.200	0.9993	Fitted	0.042	0.14
Fe 238.204	0.005 – 2.00	1.0000	Fitted	0.097	0.32
Ga 294.363	0.005 – 0.200	0.9999	FACT	0.12	0.39
K 766.491	0.010 – 0.500	0.9999	FACT	0.22	0.72
Li 670.783	0.005 – 0.200	0.9999	Fitted	0.026	0.085
Mg 279.553	0.005 – 0.200	1.0000	Fitted	0.0051	0.017
Mn 259.372	0.005– 0.200	1.0000	Fitted	0.0043	0.014
Mo 202.032	0.005 – 0.200	1.0000	Fitted	0.026	0.088
Na 589.592	0.010 – 0.500	1.0000	FACT	0.037	0.12
Ni 231.604	0.005 – 0.200	0.9998	Fitted	0.038	0.13
Pb 220.353	0.005 – 0.200	0.9999	Fitted	0.15	0.49
Sb 206.834	0.005 – 0.200	0.9998	Fitted	0.22	0.74
Sr 407.771	0.005 – 0.200	1.0000	Fitted	0.00079	0.0026
Ti 334.941	0.005 – 0.200	1.0000	Fitted	0.0031	0.010
V 309.310	0.005 – 0.200	1.0000	Fitted	0.011	0.036
Zn 213.857	0.005 – 0.200	0.9999	Fitted	0.012	0.038
Zr 343.823	0.005 – 0.200	1.0000	Fitted	0.024	0.079

Background correction

Fitted background correction (FBC) mode was selected for most elements in the ICP Expert software (Table 2). FBC automatically corrects the contribution from the background and interfering peaks that do not directly overlap the analyte peak. No manual background marker selection is needed when using FBC.

The Agilent Vista Chip III charge-coupled device (CCD) detector of the 5800 provides high-speed continuous wavelength coverage from 167 to 785 nm. The extensive wavelength range often ensures that a suitable, interference-free line can be found for most analytes, although complex samples often generate many emission lines, with some lines being too close to the analyte line of choice. When an interfering peak overlaps the spectral peak of an analyte, the Fast Automated Curve-fitting Technique (FACT) can be used to effectively resolve the interference. FACT provides real-time spectral correction using an advanced spectral modeling technique to mathematically separate the analyte signal from the raw spectrum, greatly improving detection limits of any interfered analytes.

Figure 2 shows the uncorrected spectrum of Na 589.592 nm (blue solid line) that is a combination of the analyte signal and the interfering peak from Ba 589.612 nm (red dotted line). Since the concentrations of both Na and Ba in the calibration standards are identical, the calibration for Na 589.592 nm using FBC would show good linearity, despite the interference from Ba. FACT was used to model the interfering peak from Ba 589.612 nm and resolve the analyte signal, providing accurate results for Na 589.592 nm (green solid line in Figure 2).
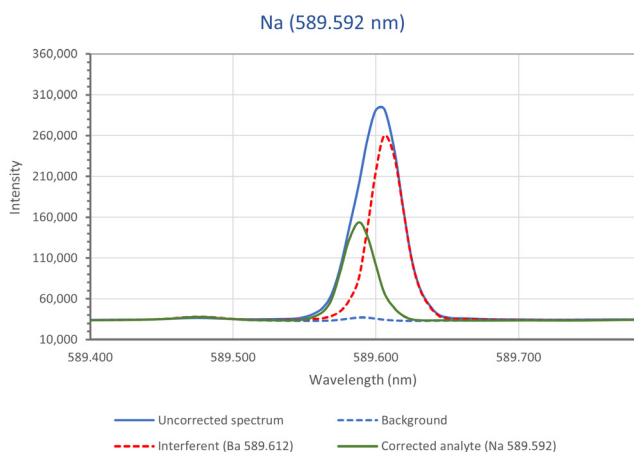
Figure 2. FACT background correction used to resolve the spectral interference of Ba 589.612 nm on Na 589.592 nm.

Limit of detection (LOD) and limit of quantitation (LOQ)

To obtain LODs and LOQs, 10 blank sample matrix solutions (28.8% AR) were analyzed during the analytical run. The LODs and LOQs were calculated as 3 and 10 times the standard deviation, respectively, of the 10 measurements. The values presented in Table 2 are the average of three LOD and LOQ results from separate tests carried out on three non-consecutive days, calculated as 1 g graphite in 50 mL solution. The LODs and LOQs for the silicon-carbon sample are 10 times of these values considering the dilution factor. (The silicon-carbon sample digests were diluted 10 times before analysis).

Elemental impurity and spike recoveries

The silicon, graphite, and silicon-carbon sample digests and spikes of the graphite and silicon-graphite samples were analyzed using the 5800 VDV ICP-OES. The average measured results and the respective spike recoveries for 25 elements are shown in Table 3. The results are corrected for the dilution factor, so are reported in mg/kg in the original solid materials. In the 99.99% graphite sample, Na was the only element present above 1 mg/kg. The concentrations of Ca, K, Fe, and Al were between 0.4 and 1 mg/kg. Trace elements, As, Ba, Be, Cd, Co, Cr, Ga, Li, Mo, Pb, Sb, and Zr were below the LODs. The 99% silicon sample contained high levels of Fe and Al (>3000 mg/kg) followed by Ca at 867 mg/kg. The concentration of the elements in the silicon-carbon sample (10% silicon and 90% graphite) were typically one-tenth of the levels measured in the silicon sample.

Spike recovery tests are an effective way to evaluate the reliability of the sample preparation method and/or the analytical method, especially when no suitable certified reference materials (CRMs) are available. As shown in Table 3, the recoveries for the graphite sample that was spiked before microwave digestion were ±10% from the expected value. The results demonstrate the effectiveness of the microwave digestion sample preparation procedure for the anode materials. Excellent spike recoveries within ±10% of the expected value were achieved for the silicon-carbon samples. These samples had been diluted 10 times and spiked at three concentrations after microwave digestion. These results confirm the accuracy of the 5800 ICP-OES method for the analysis of complex samples.

Table 3. Concentrations of elemental impurities in silicon, graphite, and silicon-carbon samples, and spike recovery data for graphite and silicon-carbon. Concentration units: mg/kg, n=3.

Element, Wavelength (nm)	Silicon	Graphite				Silicon-carbon			
	Measured Concentration	Measured Concentration	Spike Concentration*	Measured Concentration in Spiked Sample	Spike Recovery %	Measured Concentration	Spike Concentration**	Measured Concentration in Spiked Sample	Spike Recovery %
Al 396.152	3229	0.451	1.25	1.65	96	321	12.5	333	96
As 188.980	< LOD	< LOD	1.25	1.24	101	< LOD	12.5	12.4	101
Ba 455.403	19.0	< LOD	1.25	1.28	104	1.80	12.5	14.8	104
Be 234.861	0.114	< LOD	1.25	1.31	104	0.0114	12.5	12.8	103
Ca 396.847	867	0.932	1.25	2.16	98	89.1	12.5	103	100
			2.50	3.43	100		25	114	100
			5.00	5.92	100		50	139	100
Cd 214.439	< LOD	< LOD	1.25	1.30	104	< LOD	12.5	12.9	103
Co 238.892	2.74	< LOD	1.25	1.30	102	0.292	12.5	13.2	103
Cr 267.716	99.7	< LOD	1.25	1.32	106	10.3	12.5	23.4	105
Cu 327.395	38.5	0.0569	1.25	1.35	103	3.83	12.5	16.4	101
Fe 238.204	3358	0.680	1.25	1.91	98	337	12.5	349	96
Ga 294.363	< LOD	< LOD	1.25	1.24	100	< LOD	12.5	12.7	102
K 766.491	97.9	0.896	1.25	2.11	97	10.1	12.5	22.7	101
			2.50	3.42	101		25	35.9	103
			5.00	5.96	101		50	62.6	105
Li 670.783	4.77	< LOD	1.25	1.24	99	0.472	12.5	13.5	104
Mg 279.553	71.9	0.146	1.25	1.42	102	7.42	12.5	20.6	106
			2.50	2.74	104		12.5	33.6	105
			5.00	5.31	103		12.5	59.6	104
Mn 259.372	71.8	0.0131	1.25	1.31	103	7.25	12.5	20.4	105
Mo 202.032	< LOD	< LOD	1.25	1.32	106	< LOD	12.5	12.9	104
Na 589.592	32.0	1.27	1.25	2.51	99	3.89	12.5	16.4	100
			2.50	3.77	100		25	30.8	108
			5.00	6.37	102		50	107	107
Ni 231.604	90.5	0.0755	1.25	1.23	92	8.94	12.5	22.2	106
Pb 220.353	3.88	< LOD	1.25	1.32	100	0.378	12.5	12.8	100
Sb 206.834	< LOD	< LOD	1.25	1.18	100	< LOD	12.5	12.0	104
Sr 407.771	14.5	0.00370	1.25	1.30	103	1.44	12.5	14.4	103
Ti 334.941	80.9	0.0281	1.25	1.34	105	7.76	12.5	20.8	104
V 309.310	5.49	0.0390	1.25	1.26	98	0.569	12.5	13.0	100
Zn 213.857	0.612	0.0662	1.25	1.36	103	0.136	12.5	12.5	99
Zr 343.823	59.3	< LOD	1.25	1.24	99	5.53	12.5	18.3	102

*Spike concentrations, 1.25, 2.5, and 5 mg/kg, are equivalent to 0.025, 0.05, and 0.1 mg/L, respectively, of 1 g graphite in 50 mL. ** Spike concentrations were 10 times higher in silicon-carbon than for graphite due to the dilution factor.*

Long-term stability (LTS)

To check the stability of the instrument and long-term validity of the calibration, 216 measurements were completed over a 7.5-hour period without recalibration. A CCB and a CCV sample (0.05 mg/L) were measured after every 10 measurements of the spiked (0.025 mg/L) and unspiked graphite samples. The concentrations of the 19 CCV measurements were plotted against time, as shown in Figure 3. Accurate measurements within ±10% of the expected value (indicated by the dotted lines) were obtained, with %RSDs for all wavelengths below 2%, except for K 766.491 (3.31%) and Na 589.592 (3.55%).
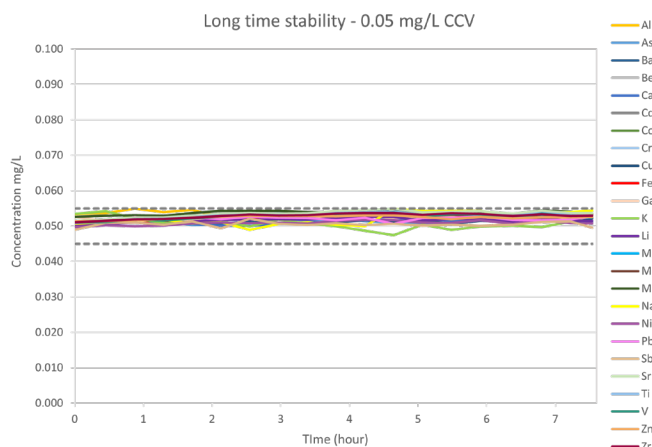
Figure 3. Long-term stability showing recoveries of the 0.05 mg/L CCV solution measured over 7.5-hours.

The precision of the 138 measurements of the spiked graphite sample was excellent over 7.5 hours, with %RSDs below 5%, as shown in Table 4.

Table 4. Long-term stability of Agilent 5800 ICP-OES over 7.5 h. %RSD of measurements of graphite samples spiked at 0.025 mg/L.

Element and Wavelength (nm)	RSD %	Element and Wavelength (nm)	RSD %
Al 396.152	1.66	Mg 279.553	1.13
As 188.980	2.10	Mn 259.372	1.68
Ba 455.403	1.84	Mo 202.032	1.74
Be 234.861	1.35	Na 589.592	1.67
Ca 396.847	1.72	Ni 231.604	1.69
Cd 214.439	1.21	Pb 220.353	2.07
Co 238.892	1.60	Sb 206.834	4.51
Cr 267.716	1.67	Sr 407.771	1.79
Cu 327.395	2.29	Ti 334.941	1.58
Fe 238.204	4.43	V 309.310	1.65
Ga 294.363	2.34	Zn 213.857	1.49
K 766.491	3.69	Zr 343.823	1.58
Li 670.783	1.14		

Conclusion

Silicon-carbon anode materials are a novel alternative to graphite-based anodes, which are typically used in lithium ion batteries (LIBs). To test the elemental purity of battery-grade anode matrices, a mixture of graphite and silicon, representing a silicon-carbon sample, and a high purity graphite sample were prepared for analysis using microwave digestion.

The Agilent 5800 VDV ICP-OES was used to quantify 25 elemental impurities in the sample digests. Excellent calibration linearity was obtained for major and minor elements over a wide calibration range and the detection limits for all elements were well below 1 mg/kg. Recoveries of all 25 elements spiked at three concentrations in the graphite sample and silicon-carbon sample were between 90 and 110%, confirming the accuracy of the sample preparation procedure and the ICP-OES method. The instrument was stable over 7.5 h, as shown by %RSDs of < 5% for all elements measured in a spiked graphite sample and a CCV solution.

The 5800 VDV ICP-OES is already widely used within the LIB industry for the quality control of component materials. The industry typically uses methods that are developed in accordance with China GB/T product quality standards, many of which recommend ICP-OES for the analysis. So, the method used in this study was based on GB/T standards for graphite negative electrode materials and silicon-carbon. The results have shown that the 5800 ICP-OES can provide the accuracy, precision, and stability needed for the analysis of trace elements in new anode materials.

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Agilent part numbers

Part number	Description
G8020-68005	Easy-fit fully demountable torch with 1.8 mm quartz injector for Agilent 5000 series ICP-OES
G8010-60256	Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet for Agilent 5000 series ICP-OES
G8010-60255	SeaSpray concentric glass nebulizer for Agilent 5000 series ICP-OES
3710034400	Peristaltic pump tubing, white/white, 12/pk
3710068200	Peristaltic pump tubing, orange/green, 12/pk
3710034600	Peristaltic pump tubing, blue/blue, 12/pk.
8500-6940	Agilent multi-element calibration standard-2A
5190-8487	Agilent 1000 ppm single element stock solution for Mo
5190-8244	Agilent 1000 ppm single element stock solution for Sb
5190-8546	Agilent 1000 ppm single element stock solution for Ti
5190-8559	Agilent 1000 ppm single element stock solution for Zr
5190-8441	Agilent 10,000 ppm single element stock solution for Rb
5190-8451	Agilent 10,000 ppm single element stock solution for Si
5190-8233	Agilent 10,000 ppm single element stock solution for Y

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