APPLICATION NOTE 000466

Determination of elemental impurities in graphite powder for lithium-ion battery anodes

Author: Thermo Fisher Scientific Inc.

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Goal

To develop a robust and reliable method for the determination of elemental impurities in graphite powder samples for lithium-ion battery anodes, using the Thermo Scientific™ iCAP™ PRO X ICP-OES Duo instrument. This note will demonstrate the performance of the method with respect to calibration linearity for 13 trace element impurities (target $R^2 > 0.999$) and quantification of these elements. It will also illustrate the robustness of the method developed through spike recovery analysis of the microwave digested samples.

Introduction

For lithium-ion batteries, the negative electrode (anode) material is generally made from graphite powder. Graphite powder is suitable for this application primarily because it is an easily molded, chemically stable, and non-metallic material with good electrical conductivity and high temperature, oxidation, and corrosion resistance. It also has a large lithium-ion diffusion coefficient with a high lithium insertion capacity and does not change volume with insertion of lithium ions. In addition, graphite powder can be modified through various oxidation and pyrolysis processes to generate a core-shell structure that can improve its charging/discharging performance and increase the anode lifetime. Graphite powder has become the main lithium-ion battery anode material in use today in smaller consumer goods, such as mobile phones, as well as in electrical vehicles.

Through optimization of the sample pre-treatment process and plasma parameters, together with rigorous selection of the most suitable analyte emission lines, a robust, accurate and reliable ICP-OES analytical method for the determination of 13 trace elements in graphite powder materials for lithium ion batteries was developed.

Experimental

Instruments and reagents

For this work, an iCAP PRO X ICP-OES Duo instrument was used (Figure 1). For sample preparation, ultrapure water (18.2 MΩ·cm resistivity), nitric acid, and hydrochloric acid (Merck) were used. Sample digestions were carried out using a microwave digestion system (ETHOS™ One, Milestone, Italy).

Figure 1. Thermo Scientific iCAP PRO X ICP-OES Duo

Calibration solution and sample preparation

Multi-element calibration solutions containing all 13 elements of interest at blank, 0.05, 0.20, and 0.50 µg/mL concentrations were prepared from a stock solution made from single element standards (1,000 µg/mL, National Standard Material Research Centre). Three raw material briquetting charcoal materials were analyzed in this study. Portions of each sample (0.5 g, accurately weighed) were mixed with 3 mL HNO_3 and 9 mL HCl in PTFE vessels and microwave digested at 190 °C for 30 minutes. After digestion was complete, the samples were diluted with ultrapure water to 50 mL and filtered prior to analysis. Microwave digestion reagent blank samples were also prepared using the same method. Finally, spike recovery tests were performed on all three briquetting charcoal samples, with each digested and diluted sample spiked at 0.20 µg/mL using the multi-element stock solution.

Instrument parameters and method optimization

The instrument configuration parameters used for the analysis are given in Table 1 and the wavelengths selected for each element are shown in Table 2.

Table 1. Instrument configuration parameters

Instrument parameter	Setting
Injection pump tubing	PVC, orange/white, i.d. 0.64 mm
Drain pump tubing	PVC, white/white, i.d. 1.02 mm
Pump speed	50 rpm
Nebulizer	Glass concentric nebulizer
Nebulizer gas flow	0.6 L/min
Spray chamber	Baffled glass cyclonic
Torch center tube	2.0 mm center tube
Observation method	Axial
RF power	1150 W
Auxiliary gas flow	0.5 L/min
Exposure time	15 s
Repeats	3

Table 2. Wavelength selection for the 13 elements analyzed

Element	Wavelength (nm)	Element	Wavelength (nm)
As	189.042	Mo	202.030
Be	313.042	Ni	231.604
Cd	214.438	Pb	220.353
Co	228.616	Sb	206.833
Cr	267.716	V	309.311
Cu	213.598	Zn	213.856
Mn	257.610		

Results and discussion

Linear calibrations (R^2 > 0.9999) were obtained for all 13 trace elements measured. The concentrations found for each element in the three raw material briquetting coal materials, calculated back to the solid samples, are presented in Table 3. The spike recovery test results for each sample are shown in Table 4. Table 4 shows that quantitative spike recoveries (from 93 to 104%) were achieved for all the trace elements measured in this study.

Table 3. Raw material briquetting charcoal sample results (mg/kg)

Sample	As	Be	Cd	Co	Cr	Cu	Mn
Briquetting charcoal 1	3.09	5.40	0.12	12.60	15.61	10.18	132.9
Briquetting charcoal 2	3.34	10.39	0.08	13.10	13.57	6.45	90.15
Briquetting charcoal 3	2.54	5.34	0.14	9.85	9.80	4.07	194.3

Sample	Mo	Ni	Pb	Sb	V	Zn
Briquetting charcoal 1	1.24	24.68	15.62	2.23	24.56	10.03
Briquetting charcoal 2	0.91	30.71	13.50	1.85	36.55	12.64
Briquetting charcoal 3	0.56	26.28	17.39	1.66	13.54	10.67

Table 4. Spike recovery results

	As	Be	Cd	Co	Cr	Cu	Mn
Sample 1 (µg/mL)	0.031	0.0540	0.001	0.126	0.156	0.102	1.329
Spike result (µg/mL)	0.218	0.257	0.189	0.321	0.355	0.297	1.532
Spike (µg/mL)	0.200	0.200	0.20	0.200	0.200	0.200	0.200
Spike recovery (%)	94	101	94	97	99	98	102
	As	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Mn**
Sample 2 (µg/mL)	0.033	0.104	0.001	0.131	0.136	0.065	0.902
Spike result (µg/mL)	0.225	0.312	0.192	0.332	0.343	0.263	1.107
Spike (µg/mL)	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Spike recovery (%)	96	104	96	101	103	99	103
	As	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Mn**
Sample 3 (µg/mL)	0.025	0.053	0.001	0.099	0.098	0.041	1.943
Spike result (µg/mL)	0.221	0.254	0.193	0.294	0.298	0.234	2.132
Spike (µg/mL)	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Spike recovery (%)	98	100	96	98	100	97	95

	Mo	Ni	Pb	Sb	V	Zn
Sample 1 (µg/mL)	0.012	0.247	0.156	0.022	0.246	0.100
Spike result (µg/mL)	0.210	0.434	0.345	0.223	0.441	0.288
Spike (µg/mL)	0.200	0.200	0.200	0.200	0.200	0.200
Spike recovery (%)	99	93	94	101	97	94
	Mo	**Ni**	**Pb**	**Sb**	**V**	**Zn**
Sample 2 (µg/mL)	0.009	0.307	0.135	0.019	0.366	0.126
Spike result (µg/mL)	0.212	0.502	0.324	0.222	0.568	0.316
Spike (µg/mL)	0.200	0.200	0.200	0.200	0.200	0.200
Spike recovery (%)	101	97	94	102	101	95
	Mo	**Ni**	**Pb**	**Sb**	**V**	**Zn**
Sample 3 (µg/mL)	0.006	0.263	0.174	0.017	0.135	0.107
Spike result (µg/mL)	0.203	0.455	0.369	0.220	0.330	0.297
Spike (µg/mL)	0.200	0.200	0.200	0.200	0.200	0.200
Spike recovery (%)	99	96	98	102	97	95

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Conclusion

This application note has demonstrated the performance of the iCAP PRO X ICP-OES Duo instrument for quantitative trace element impurity analysis in graphite powder samples (derived from briquetting coal) used for lithium-ion battery anode production. Using the ASTM D6357-2004 and GB/T24533-2009 (Appendix H) standards as a guide, a robust sample preparation method based on microwave digestion of the samples was developed. Concentrations were determined for all 13 trace elements in the three raw material briquetting charcoal samples, and the robustness of the analysis was confirmed by the achievement of quantitative spike recoveries of the measured elements (in the range 93 to 104%).

The iCAP PRO X ICP-OES Duo provides the advantages of high sensitivity, good stability, fast analysis speed and low operating costs required for all aspects of elemental analysis in the lithium ion battery workflow. From quantifying lithium concentrations in ores and brine to routinely confirming the composition of cathode active materials in a QA/QC environment, the iCAP PRO X ICP-OES Duo offers the performance and flexibility required to meet the analytical demands of this rapidly growing sector.

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