



Recent Advances in Elemental Analysis for the Lithium Ion Battery Supply Chain

Introduction

The lithium ion battery supply chain extends from mines and refiners to makers of cells and battery packs to original equipment manufacturers (OEMs). Determining exactly what elements are present in a given material, in exactly what amounts, can play a critical part in quality control at various processing phases.

This paper outlines requirements for elemental analysis of processed materials at selected steps in the chain, focusing on graphite, lithium salts, and cathode components. It presents the latest advances in some traditional measurement solutions for these materials, such as ICP-OES analysis.

However, the paper also highlights two proven analytical technologies not yet commonly used for lithium ion battery applications: ED-XRF and ETV-ICP-OES. These offer exciting new capabilities and advantages — such as speed, convenience, and precision — that recommend them for wider application in the battery industry.



Analyzing graphite

The anodes of most lithium ion batteries are constructed of the mineral graphite, or of other carbon materials. Designs usually demand graphite purity of better than 99.95%. During production, control of that purity is required at several steps in the supply chain, including mines, refiners, and battery manufacturers. Also, impurities, present in trace amounts in the per million (ppm) range— must be controlled, to avoid degradation of battery performance.

Precise elemental analysis is required. Three different analytical technologies may be used for this application:

- Inductively coupled plasma mass spectrometry (ICP-MS)
- X-ray fluorescence spectrometry (XRF)
- Inductively coupled plasma optical emission spectrometry (ICP-OES) with electrothermal vaporization (ETV)

Graphite analysis via ICP-MS

ICP mass spectrometry is widely used for this analysis. It delivers good sensitivity and acceptable accuracy for this applications.

However, the performance comes at the cost of considerable difficulties that users may encounter in sample preparation.

Typically, a graphite sample is mineralized with nitric acid in a microwave digestion unit, any residue filtered and diluted with water. Another technique involves the ashing of the sample, then fusion with lithiumtetraborate and dissolution with nitric acid and water. The solution, then, can finally be evaluated in the ICP-MS analyzer. Both digestion methods are time-consuming,. While the first can be automated to a certain extent, the second is largely manual. Dissolution using nitric acid and a microwave oven may not dissolve all constituents contained in the sample, ashing at 700° C may lose volatile elements. Also, it may introduce sample contamination via reagent additions.

Graphite analysis via XRF

Rather than subjecting samples to a high-temperature plasma, as in ICP-MS or ICP-OES, XRF spectrometry excites the atoms in a sample material using an X-ray tube.

XRF technology thus possesses several advantages for graphite analysis. It's nondestructive, and won't lose volatiles before analysis can be completed. Compared to most ICP instruments, XRF

analyzers are also relatively simple, easy to operate, and fast — often calling for little or no sample preparation. And they're significantly less expensive than ICP-MS models. On the other hand, low X-ray yields can make it difficult for the technology to analyze lighter elements. These may include sodium, sometimes an impurity of interest.

So use of XRF may not be indicated where high-purity graphite analysis is required. However, it can provide an excellent solution where quick screening of graphite material to ppm levels is all that is needed.

A higher amount of impurities in graphite comes from its natural resources, therefore a higher interest is to determine the larger concentrations like those from Al_2O_3 , SiO_2 , CaO , Fe_2O_3 but also of S in the base material. Other oxides and elements can be determined simultaneously. The illustrations 1 and 2 show example correlations for the analysis of Al_2O_3 and SiO_2 in pure graphite to demonstrate the capabilities of the SPECTRO XEPOS ED-XRF.

Graphite analysis via ICP-OES with ETV

Perhaps the most efficient and reliable method for high-purity graphite analysis combines a proven analytical solution with sample introduction technology that may be unfamiliar to many users in the battery supply chain.

Electro Thermal Vaporization (ETV), a sample introduction technique, which can be used in conjunction with an ICP-OES instrument, has been employed for some

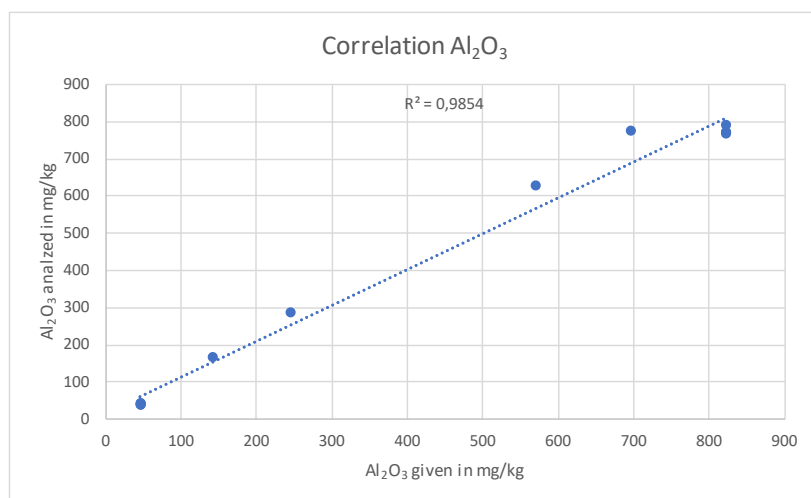


Illustration 1: Correlation of Determination of Al_2O_3 Content in Graphite using SPECTRO XEPOS ED-XRF.

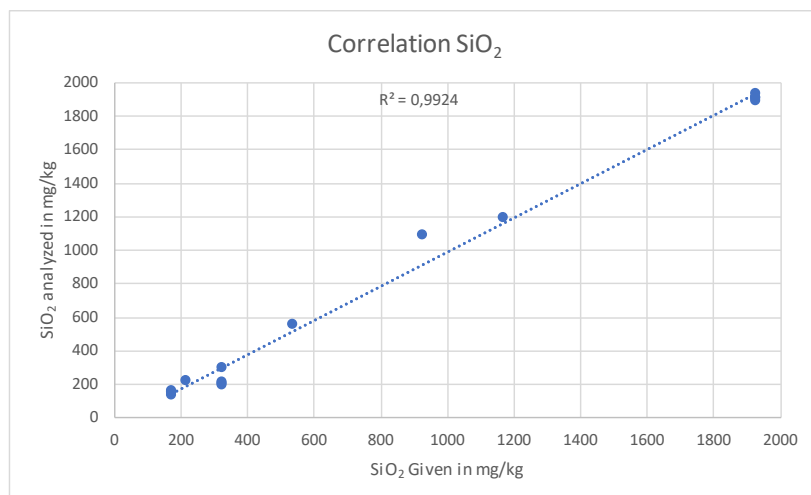


Illustration 2: Correlation of Determination of SiO_2 Content in Graphite using SPECTRO XEPOS ED-XRF.



time in various applications where difficult-to-digest samples are encountered. For example, the combination is utilized to analyze trace elements in ceramic materials like silicon carbide or aluminum oxide, to measure impurities in high purity copper but also differentiating sulfur species in coal. Its analytical characteristics make ETV-ICP-OES extremely well suited for the analysis

of pure carbon and graphite samples. However, the technology has been limited by the somewhat cumbersome technique and the need for a knowledgeable, skilled operator. And few current ICP-OES systems possess the capabilities of simultaneous analysis, transient measurement, and advanced software necessary for the evaluation of the transient signals.

Fortunately, recent advances in methodology and automation have made ETV easier to use and more adapted to higher-productivity applications. And one ICP-OES instrument that can handle the application's analytical requirements is the SPECTRO ARCOS ICP-OES analyzer from SPECTRO Analytical Instruments.

Equipment and operation

For graphite analysis, the benchtop analyzer may be staged with an ETV system consisting of a 50-position autosampler, a robotic sample handler, and a electrically heated graphite furnace.

To begin a sample run, the operator prepares the 50-place carousel tray on the autosampler, weighing a small amount (usually 10-500 mg) of powdered sample into each a graphite boat. The boats are placed on the sample tray; then the automated process is started. Using tweezers, the robot transfers the first filled boat into the furnace, positioning it at a fixed spot. The system heats the furnace applying a predefined temperature program (max temperature 3000° C / 5432° F), transforming the impurities in the graphite into volatile species using freon as a reaction gas. Using argon as



a carrier gas the generated dry aerosol is transferred via a PTFE tube into the ARCOS instrument's plasma for ICP-OES analysis. After the analysis, which requires only 2-3 minutes, the robot retrieves the boat from the furnace and returns it to the tray, moving on to handle the next sample. All components are accessible for easy operation and maintenance. Gas flows and temperatures are electronically controlled.

Versus ICP-MS: increases sensitivity, while saving time, trouble, costs

When compared to ICP-MS instruments, the currently most popular technique for graphite analysis, ETV-ICP-OES technology is faster and simpler; it also costs the same or less to purchase, and less to operate.

The method's great advantage: analysis by ETV means that the ICP system is able to perform direct analysis of essentially the entire sample, without dilution or loss. This delivers a substantial increase in analytical sensitivity— yielding extremely low limits of detection (LODs). So the system can routinely detect trace element

concentrations within a graphite sample down to below single digit parts per billion (ppb) level. And the typical precision of the measured intensity integrals demonstrates less than 3% relative standard deviation (RSD). These outcomes are clearly superior to the performance achievable with an ICP-MS instrument. Precision and limits of detection achievable using ETV-ICP-OES are shown in the accompanying table. (See Table 1 and 2).

Also, technologies such as glow discharge mass spectrometry (GD-MS) require continuous hands-on operation by lab personnel. Instead, ETV-ICP-OES allows unattended, automated elemental analysis of multiple samples. So labs can deliver much greater throughput and productivity with much less time and effort for lab personnel.

In summary, comparison to ICP-MS analysis and its usual preparation methods — digestion or ashing — demonstrates many ETV-ICP-OES advantages:

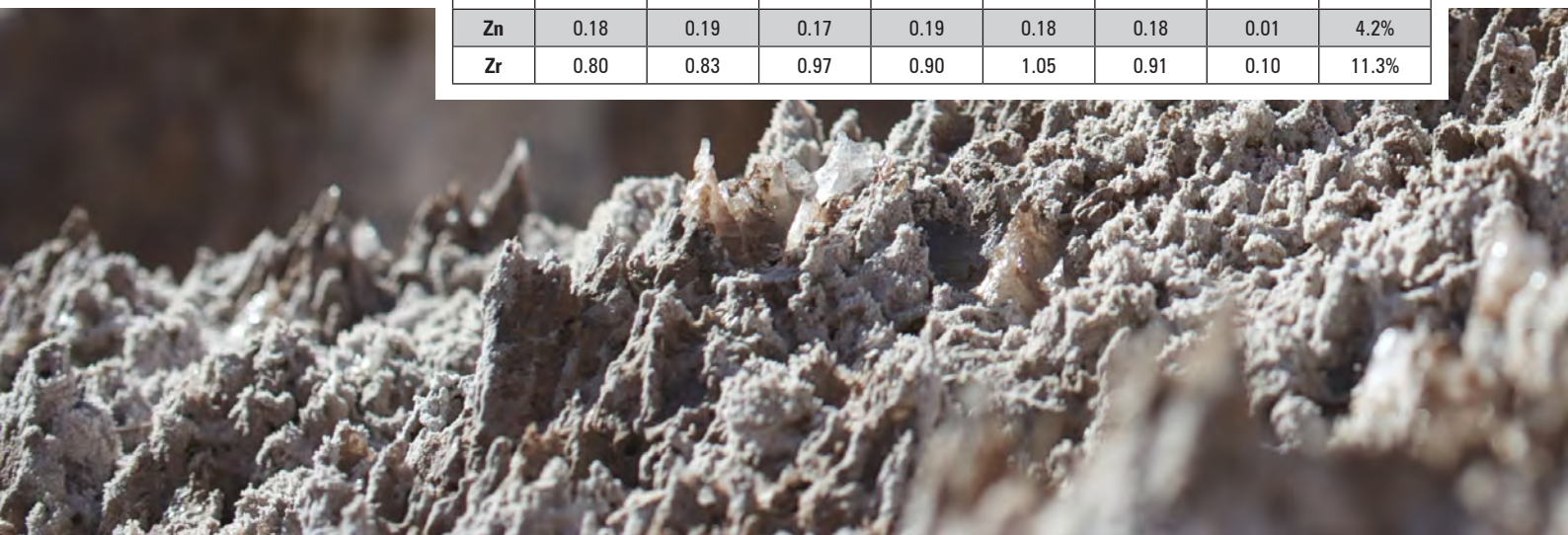
- Unmatched sensitivity — with LODs down to below ppb levels
- No fussy, time-consuming chemical digestion
- No complex fusion and/or mixed acid techniques
- No reagents (eliminating possible contamination sources)
- No loss of volatile elements
- Greatly reduced risk of sample preparation errors
- Automation (autosampler) for high sample throughput
- Substantial overall time savings
- Increased ease of handling
- Significantly lower costs of analysis

Element	LOD (3 σ) [μ g/kg]	Element	LOD (3 σ) [μ g/kg]	Element	LOD (3 σ) [μ g/kg]
Ag	0,67	Ga	3	S	1,33
Al	0,07	In	3	Sb	3
As	0,67	K	3	Sn	6
B	1,33	Li	0,30	Sr	0,07
Bi	3	Mg	0,67	Ti	0,67
Ca	0,67	Mn	0,07	Tl	3
Cd	0,07	Mo	0,67	V	3
Co	0,30	Na	0,67	W	6
Cr	0,30	Ni	0,67	Zn	6
Cu	0,30	P	0,67	Zr	0,67
Fe	0,30	Pb	0,67		

Table 1: Typical LODs (3 σ) achievable in graphite matrix

Table 2: Short term precision test of a high purity graphite sample

Element	1 [mg/kg]	2 [mg/kg]	3 [mg/kg]	4 [mg/kg]	5 [mg/kg]	Average	SD	RSD
Al	1.66	1.79	1.70	1.77	1.76	1.74	0.05	3.2%
Ba	0.85	0.86	0.86	0.89	0.88	0.87	0.02	1.8%
Be	0.04	0.04	0.04	0.04	0.04	0.04	0.00	2.0%
Ca	0.37	0.37	0.21	0.32	0.34	0.32	0.07	21.3%
Cd	0.08	0.09	0.09	0.09	0.10	0.09	0.01	9.1%
Co	0.09	0.09	0.09	0.08	0.08	0.09	0.00	3.1%
Cr	0.91	0.95	0.77	0.78	0.78	0.84	0.09	10.2%
Cu	0.11	0.09	0.10	0.14	0.14	0.12	0.02	18.6%
Fe	5.10	4.31	4.02	4.33	4.34	4.42	0.40	9.1%
K	0.16	0.18	0.20	0.15	0.16	0.17	0.02	11.1%
Li	0.19	0.20	0.22	0.22	0.24	0.21	0.02	7.6%
Mg	0.38	0.40	0.36	0.38	0.37	0.38	0.01	3.6%
Mn	0.10	0.08	0.09	0.09	0.09	0.09	0.01	6.8%
Mo	0.17	0.28	0.26	0.22	0.16	0.22	0.05	24.5%
Na	0.85	0.99	0.59	0.75	0.73	0.78	0.15	19.0%
Ni	1.48	1.54	1.51	1.57	1.58	1.53	0.04	2.9%
P	1.53	1.09	1.91	1.91	1.48	1.58	0.34	21.8%
Pb	0.44	0.41	0.50	0.38	0.43	0.43	0.04	9.6%
Sb	1.49	1.54	0.80	1.06	1.36	1.25	0.31	24.8%
Sn	1.06	1.16	1.24	1.09	1.21	1.15	0.08	6.8%
Sr	0.19	0.19	0.19	0.20	0.19	0.19	0.00	1.9%
Te	1.33	1.59	1.98	1.81	1.93	1.73	0.27	15.5%
Te	1.95	1.74	1.70	1.42	1.44	1.65	0.22	13.3%
Ti	0.76	0.70	0.79	0.77	0.56	0.72	0.09	12.9%
Ti	0.74	0.65	0.74	0.68	0.67	0.70	0.04	6.4%
V	1.63	1.86	1.79	2.26	1.34	1.78	0.34	19.0%
W	4.48	4.47	6.42	5.05	5.81	5.25	0.85	16.3%
Zn	0.17	0.18	0.17	0.17	0.18	0.17	0.01	3.7%
Zn	0.18	0.19	0.17	0.19	0.18	0.18	0.01	4.2%
Zr	0.80	0.83	0.97	0.90	1.05	0.91	0.10	11.3%



Versus XRF: much greater sensitivity

As opposed to XRF analysis, ICP-OES/ETV is destructive — it completely consumes the impurities in the sample in the high-temperature plasma. Also, using ETV equipment and controlling various procedural parameters may demand a somewhat higher level of skill than operation of a simple XRF instrument.

However, compared to XRF, ICP-OES/ETV demonstrates extremely high sensitivity (and thus low LODs), for readings that are superior by three orders of magnitude — ppb for the ICP results, versus only ppm for an XRF analyzer. XRF is recommended for quick screening applications. For high-purity graphite analysis, ICP-OES/ETV is clearly the better choice.

Analyzing lithium salts and cathode materials

The cathodes of lithium ion batteries are composed of a lithium salt, such as lithium cobalt oxide (LiCoO_2) or LiNiMnCoO_2 . Depending on the battery material type, in addition to lithium a variety of other elements and oxides, such as iron (Fe),

titanium (Ti), Al or the phosphate (PO_4) — are combined as main components. In addition, these batteries' electrolytes are composed of a lithium salt (e.g. LiPF_6 Lithium Hexafluorophosphate) dissolved in an organic solvent (e.g. ethylene carbonate, dimethyl carbonate, or diethyl carbonate)

Various aspects of a battery's performance, safety and cost depend on the composition and the material's stoichiometry: the proportional relationship of each component to the others. Elements, composition and limits vary by battery type and by manufacturer, but formulas normally call for purities greater than 99.9%.

So processors demand precise elemental analysis to accurately determine the main components, but also analyze impurities at low levels; and ensure that the latter don't exceed specified limits.

The industry standard for these applications is ICP analysis. XRF will also be briefly considered below. For ICP analyzers, samples are first prepared via standard laboratory digestion to obtain an aqueous solution for analysis.



Salt and cathode material analysis via ICP-OES

In cathode materials, the composition of the main elements, lithium, and depending on the type additional main elements like Co, Fe, Mn, Ni, P and Ti need to be determined with extremely high precision and accuracy. Likewise, impurities need to be determined — for most elements, to less than 10 ppm.

ICP-OES delivers good results for the analyses necessary for cathode and electrolyte materials processing. Analyzers may exhibit important differences in factors such as sensitivity, precision, speed of analysis, ease of use, and cost of ownership. (See The analyzers section below.) However, a well-designed ICP-OES analyzer can analyze the materials' main components with a high degree of precision. And it can identify metal impurities at the required ppm levels for ensured quality control during processing.

A radial revolution

A recent development in ICP-OES analysis is the significant improvement in some models' performance using radial plasma observation. Here, the SPECTRO ARCOS — the flagship ICP-OES instrument from SPECTRO Analytical Instruments, available in both axial and radial models — has developed new capabilities.

Traditionally, radial observation delivers higher precision, while axial observation offers higher sensitivity. However, the sensitivity of the SPECTRO ARCOS analyzer's radial model is now sufficiently high that it can produce good results for trace element analysis in cathode material and lithium salts. This means many users can choose a radial model for their complete battery material analysis work — thus avoiding additional analysis using the axial plasma observation technique.

Since the material can be rather line rich, the high resolution the SPECTRO ARCOS provides over a wide wavelength range combined with advanced background correction techniques like smart background correction (SBC) additionally improves the performance, particularly the accuracy at low concentration levels.

The accompanying charts show for a sample analysis of lithium carbonate (Li_2CO_3), lithium nickel cobalt manganese oxide (LiNiCoMnOx), and nickel cobalt manganese (NiCoMn) hydroxide materials the limits of detection and the precision determined for the selected elements. Excellent sensitivity for the determination of low concentration levels and high precision for the main components was obtained.



Table 3: ICP-OES Analysis of trace elements in Lithium Carbonate and LODs (3σ) obtained in this matrix

Element	Wavelength [nm]	Measured Value [mg/kg]	Detection Limit \pm [μ g/kg]
Al	167.078	0.91	3.8
Ca	393.366	2.03	2.1
Cd	214.438	< DL	10.2
Cr	267.716	0.16	31.6
Cu	327.396	0.095	150
Fe	259.941	2.34	21.9
K	766.896	2.09	956
Mg	280.27	2.38	1.9
Mn	257.611	0.40	7
Na	589.592	186	439
Ni	221.648	0.10	49.8
Pb	168.215	< DL	179
S	180.731	243	60
Si	251.612	14.3	169
Zn	206.200	0.086	16.1

\pm 10 replicates, dilution factor 25

Table 4: High Precision ICP-OES Analysis of Li in Lithium Carbonate

Element	Wavelength [nm]	Expected range [%]	Obtained RSD [%]
Li	670.78	>18.5*	0.074

*Corresponds to >98.5% Li_2CO_3
Internal Standard: 20 mg/L Y

Table 5: ICP-OES trace analysis Lithium Nickel Cobalt Manganese Oxide and LODs (3σ) obtained in this matrix

Element	Wavelength [nm]	Measured Value [mg/kg]	Detection Limit \pm [μ g/kg]
Al	167.078	17.0	31.1
Ca	393.366	18.2	3.3
Cd	226.502	1.01	520
Cr	283.563	1.18	60.4
Cu	324.754	< DL	134
Fe	259.941	7.90	131
K	766.896	10.6	1964
Mg	280.27	46.1	14.4
Na	589.592	200	178
Pb	168.215	< DL	884
S	180.731	1523	1081
Si	288.158	16.6	374
Zn	206.200	1.46	92.8

\pm 10 replicates, dilution factor 40.

Table 6: High Precision ICP-OES Analysis of the Main Components in Lithium Nickel Cobalt Manganese Oxide

Element	Wavelength [nm]	Expected range [%]	Obtained RSD [%]
Co	228.616	11 - 13	0.042
Li	670.78	7.3 - 7.5	0.033
Mn	294.921	16 - 18	0.051
Ni	231.604	29 - 31	0.039

Internal Standard: 15 mg/L Y

Table 7: ICP-OES trace analysis of Nickel Cobalt Manganese Hydroxide and LODs (3σ) obtained in this matrix

Element	Wavelength [nm]	Measured Value [mg/kg]	Detection Limit \pm [μ g/kg]
Al	167.078	1.08	19.7
Ca	393.366	12.9	2.3
Cd	226.502	1.00	294
Cr	283.563	1.48	34.3
Cu	324.754	< DL	116
Fe	259.941	3.32	331
K	766.896	3.54	2149
Mg	280.27	56.5	8.2
Na	589.592	163	479
Pb	168.215	< DL	1170
S	180.731	1685	1508
Si	288.158	12.9	354
Zn	206.200	0.43	66.2

\pm 10 replicates, dilution factor 40.

Table 8: High Precision ICP-OES Analysis of the Main Components in Nickel Cobalt Manganese Hydroxide

Element	Wavelength [nm]	Expected range [%]	Obtained RSD [%]
Co	228.616	11 - 13	0.039
Mn	294.921	16 - 18	0.052
Ni	231.604	29 - 31	0.062

Internal Standard: 15 mg/L Y

Cathode and lithium salt analysis via XRF

Where precise lithium concentrations need to be determined, XRF analyzers fall short. However, for certain other battery processing work, XRF outdoes ICP-OES in speed, simplicity, and ease of operation — often calling for little or no sample preparation. And it's significantly less expensive than ICP-MS or ICP-OES technologies.

XRF is best applied for fast screening tasks. For example, it can quickly distinguish between lithium iron phosphate (LiFePO_4) and lithium manganese oxide (LiMn_2O_4). And in the popular cathode material lithium nickel manganese cobalt (NMC 811), the ratios between cobalt, manganese and nickel are critical: a ratio of eight parts nickel, one part manganese, and one part cobalt must be maintained. A well-calibrated XRF analyzer can swiftly determine the stoichiometry of a given sample, and confirm that this ratio holds.

The analyzers

As seen above, precise analytical solutions are required to ensure material quality (and ultimately battery performance) at several steps in the lithium ion battery supply chain. However, many analyzer suppliers offer suitable instruments for only one or two battery applications.

By contrast, SPECTRO Analytical Instruments has solutions across the supply chain. Ideal performers for the battery world include its SPECTRO ARCOS and SPECTRO XEPOS analyzers.

SPECTRO ARCOS

The SPECTRO ARCOS ICP-OES analyzer is ideal for the most demanding elemental analyses in battery-related industry and research. Leading the SPECTRO ICP-OES line, it offers numerous technological and user-centric advantages.

Unlike competing ICP-OES instruments, the analyzer is designed with a unique optical system to minimize light loss and stray-light, for lower limits of detection across a wider spectral range. It also provides high





resolution, exceptional performance on the line-rich matrixes found when analyzing lithium cathode materials with many line rich elements included at higher concentration levels. Also, SPECTRO ARCOS is available with axial- or improved, high-capability radial-view plasma observation — plus a unique MultiView option featuring both capabilities in a single instrument. Its innovative, solid-state generator provides the industry's highest power in an energy-efficient package.

SPECTRO ARCOS features a sealed gas purification system to eliminate expensive gas purging. And its exclusive air-cooled interface and generator avoids expensive, trouble-prone external water cooling systems. Altogether, its design ensures exceptionally low operating costs over a long, reliable service life.

Finally, its advanced optical, fast readout with transient measurement capabilities and software technologies make SPECTRO ARCOS one of the few ICP-OES analyzers that can combine with an ETV sample introduction system. As detailed above, this allows unsurpassed sensitivity, speed, efficiency, and reliability in determining

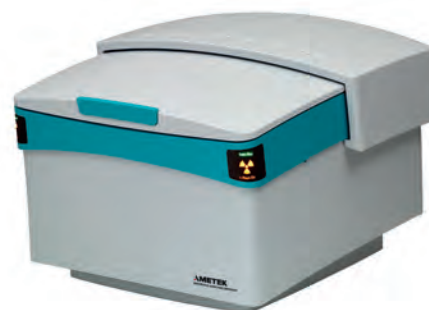
graphite purity for advanced quality control. And its improved design makes it possible to use a radial-plasma observation for analysis of cathode materials and electrolyte salts, avoiding taking advantage of the technique's high precision, avoiding analytical re-work using the axial observation technology.

SPECTRO XEPOS

The SPECTRO XEPOS energy dispersive X-ray fluorescence (ED-XRF) spectrometer redefines its category with exceptionally improved levels of performance. For example, it offers up to 3X better precision and accuracy for analysis of trace elements and components — such as battery cathode metals and salts components.

The instrument features unique adaptive excitation, tube design, and high-count throughput detection system technologies for lower LODs than many other XRF systems can achieve, which is for example important when screening graphite to be used as anode material.

For cathode and lithium salt manufacturing applications that demand fast, easy, simple, ultra-affordable screening for elemental concentrations and stoichiometry, SPECTRO XEPOS is an excellent choice.



Global support and solutions

Uninterrupted production is critical at many steps in battery manufacture and related businesses. AMECARE performance services, with more than 200 support engineers in 50+ countries, can ensure maximum uptime and productivity for SPECTRO instruments. Also, as part of the global electronic device manufacturer AMETEK, SPECTRO Analytical can offer other worldwide resources. AMETEK companies produce electrothermal analyzers and other high-end instrumentation that can provide innovative solutions for critical issues in the battery supply chain.

Conclusion

All along the lithium ion battery supply chain, accurate analysis of processed materials can make critical contributions to quality control. Standard analytical technologies such as ICP have undergone recent improvements that merit careful consideration. In addition, technologies already proven in other fields — such as ETV-ICP-OES and XRF — may provide speed, convenience, precision, and other advantages that can offer exciting new possibilities in ensuring battery performance, safety, and affordability.

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