Varied Sample Types and Multielement Screening Using Agilent ICP-MS in Helium Mode

Agilent ICP-MS systems are used to analyze an almost unimaginable variety of sample types. In issue 91 of the Agilent ICP-MS Journal, we showcase ICP-MS applications in lithium-ion battery manufacturing and the development of alternative (non-animal) protein sources.

In both cases, monitoring the levels of a wide range of trace and higher-level elements is essential to understanding the source of contaminants and their impact on the performance and safety of the final product. The high and variable sample matrices, combined with the low levels of many contaminant elements, make helium (He) cell mode an invaluable part of the methodology.

Multi-element He mode analysis is also a key part of applications where trace element fingerprints are used to differentiate samples, for example to help counter food fraud. In the work reported in this issue, an Agilent 7850 ICP-MS with Agilent MPP chemometrics software was used to identify the origin of high-value Indian tea varieties.

Figure 1. Agilent 7850 ICP-MS with Agilent SPS 4 autosampler — a powerful combination used for the routine analysis of typical sample-types.

ICP-MS for Trace Level Analysis of Contaminants in Materials Used in Lithium-Ion Battery Manufacturing

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Lithium-ion rechargeable batteries

Demand for lithium-ion (Li-ion) rechargeable batteries (LIBs) is growing rapidly due to their widespread use in portable electronic devices and electric vehicles (EVs). There is also a growing need for battery storage associated with renewable electricity generation. LIBs currently provide the best combination of cost, capacity, charging speed, and lifetime.

A LIB consists of four components, the anode, cathode, electrolyte, and separator (Figure 1). During LIB charging, Li ions are released from the cathode, migrate through the electrolyte, and are stored in the anode. During discharge, the reverse process occurs, with Li ions migrating from the anode to the cathode.

Various Li salts are used in the LIB electrolyte, including lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), and lithium perchlorate ($LiClO_4$). Salts such as lithium bis(fluorosulfonyl)imide (LiFSI) are also used to improve performance.

The cathode active material (CAM) is typically Li combined with a transition metal oxide such as cobalt oxide (LCO), nickel cobalt aluminum oxide (NCA), or nickel cobalt manganese oxide (NCM or NMC). Alternative cathode materials (not based on cobalt) include lithium iron phosphate (LFP) and lithium manganese oxide (LMO). Since the early days of LIB development, graphite has been used almost exclusively for the anode material in all LIBs, with the Li ions being stored in the lithiated graphite compound LiC_6.

The performance, lifetime, and safety of a LIB are affected by the electrochemical properties and composition of the anode, cathode, and electrolyte. Monitoring elemental contaminants in these components and the raw materials they are made from is therefore essential for manufacturing quality control and to support development of new battery materials.
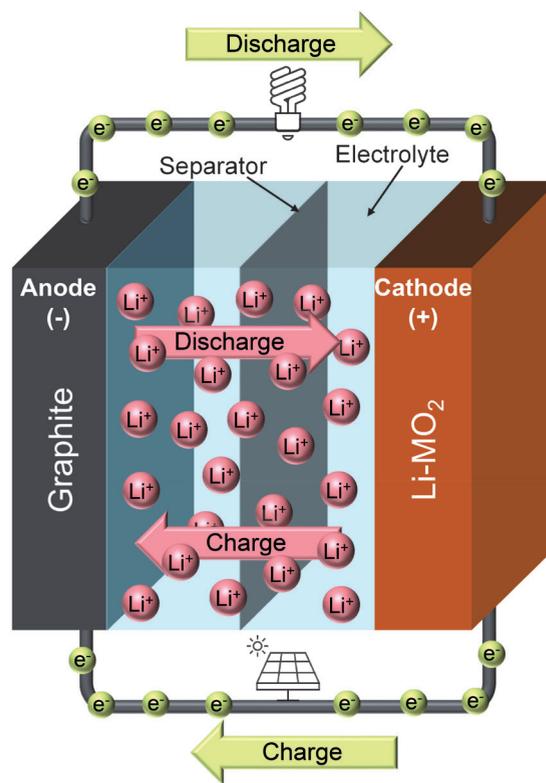
Figure 1. Schematic of a Li-ion battery showing migration of Li$^+$ ions during charging and discharging cycles.

LIB raw material suppliers and battery manufacturers require accurate analytical methods to determine a range of elements such as Fe, Ca, Mg, Cu, Zn, Si, Al, and Na in LIB raw materials and components. In China, standard methods YS/T 928.4, GB/T 24533-2019, GB/T 26300-202, and GB/T 26008-2020 currently specify ICP-OES as the recommended technique for determining contaminant elements. Cathode material manufacturers aim to control the critical contaminant elements (Fe, Cu, Zn, Pb) at below single mg/kg (ppm) levels in the solid. But ICP-OES does not provide low enough detection limits for labs that are interested in quantifying contaminants at the low levels required to investigate new and advanced battery materials.

Chinese standard method GB/T 26125 specifies ICP-MS as one of the recommended analytical techniques for hazardous heavy metals such as Cd, Hg, and Pb. It would be beneficial for analysts in the battery industry to be able to use the much lower detection limits and spectral simplicity of ICP-MS for trace-level analysis of other contaminants, particularly those that are difficult by OES.

Trace contaminant analysis using Agilent ICP-MS

All Agilent ICP-MS systems include Ultra High Matrix Introduction (UHMI) aerosol dilution to enable samples up to % levels of dissolved solids to be introduced. UHMI simplifies analytical workflows by reducing the amount of sample dilution required before analysis, while also minimizing matrix suppression, enhancing ionization, and reducing spectral overlaps. Agilent ICP-MS systems also use the ORS[4] collision/reaction cell (CRC), which is optimized for helium (He) collision mode with kinetic energy discrimination (KED). He KED removes multiple polyatomic ion overlaps in complex and variable sample matrices, using a single set of consistent conditions.

For intense background overlaps on difficult elements Si, Ca, and Fe, an optional H_2 cell gas line provides even more effective interference control (Figure 2).
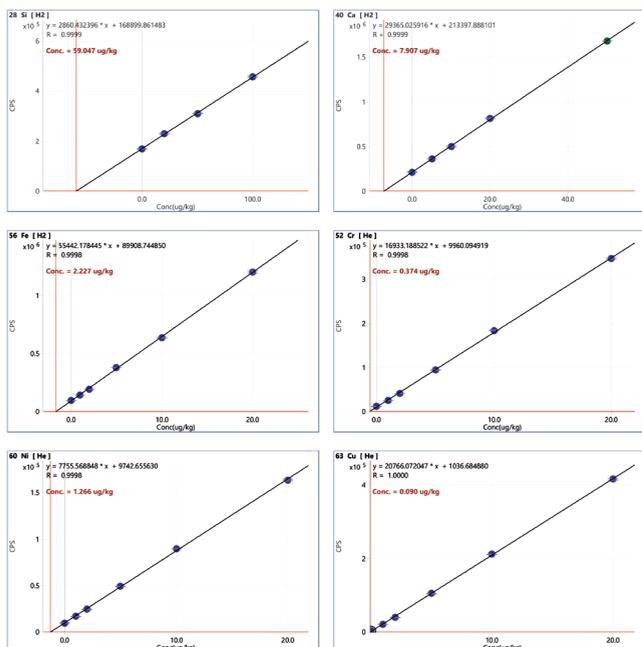

Figure 2. Standard addition calibrations for trace element contaminants in LIB electrolyte salt, LiFSI, measured using the Agilent 7900 ICP-MS.

The combination of robust plasma conditions (CeO/Ce ratio <1%), UHMI, and He KED provides effective control of spectral overlaps, enabling Agilent ICP-MS systems to fully characterize trace level contaminants (Figure 3) (2).

A He mode Quick Scan acquisition provides full mass data for every sample, with only an extra two seconds of acquisition time per sample. Quick Scan data provides identification of unexpected contaminants, as illustrated for the NCM cathode material shown in Figure 3. Data is processed using IntelliQuant to provide semiquantitative concentrations without element-specific standards.
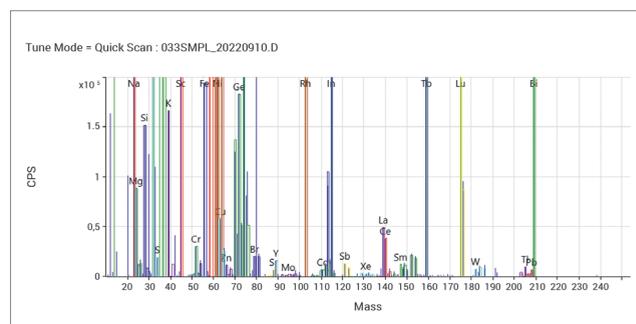

Figure 3. Agilent 7900 He mode Quick Scan spectrum showing trace elements in digested Li Ni Co Mn (NCM) cathode material. Intense peaks include Co and Ni, and internal standards, Sc, Ge, Rh, In, Tb, Lu, and Bi.

Triple quadrupole ICP-MS for even lower DLs

Single quadrupole 7850 and 7900 ICP-MS systems provide the low detection limits needed to comply with current industry requirements for LIB production.

For advanced battery manufacturing and for research into new materials and processes, an Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) provides even lower detection limits. ICP-QQQ is especially useful for analytes that are affected by matrix-based spectral overlaps (3).

References

1. Accurate ICP-MS Analysis of Elemental Impurities in Electrolyte Used for Lithium-Ion Batteries, Agilent publication, 5994-5363EN

2. ICP-MS Analysis of Trace Elements in LIB Cathode Materials, Agilent publication, 5994-5509EN

3. Quantifying Metal Impurities in Li-Ion Battery Raw Materials by ICP-MS/MS, Agilent publication, 5994-5341EN

Characterizing the Elemental Content of Alternative Proteins Using Helium Mode ICP-MS with IntelliQuant

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Alternative—non-animal—sources of protein

In a recent Agilent webinar, reviewed in Journal issue 90 (*1*), it was noted that demand for alternative (non-animal) protein sources is projected to increase rapidly. Cultured meat is one possible protein source being investigated (*2*), while foods based on plant, fungi, algae, and insect protein are also being developed or are already available.

The sample preparation methods, analytical techniques, and quality control (QC) protocols defined in existing food quality and safety regulations, such as FDA EAM 4.7, can be applied to novel foodstuffs (*2*). But new food types and manufacturing processes can lead to consumers being exposed to unexpected contaminants that may not be covered in existing regulations. An analytical technique that can provide full elemental characterization, as well as accurate determination of all regulated elements, would therefore be invaluable for food producers, regulators, and consumers.

Elemental screening using He mode ICP-MS

Agilent ICP-MS instruments—whether single or triple quadrupole—include the unique combination of an exceptionally robust plasma (CeO/Ce ratio <1.5%), and ORS[4], the most effective helium (He) collision mode for interference control. The robust plasma provides unmatched matrix decomposition, ensuring long-term stability and minimal routine maintenance, while also improving ionization, reducing the formation of many spectral overlaps, and minimizing matrix suppression.

The Agilent ORS[4] collision/reaction cell uses He mode with kinetic energy discrimination (KED) to provide a simple, universal method to filter out matrix-derived polyatomic ions. He KED on the ORS[4] improves accuracy and minimizes variability between sample types, while also giving access to all preferred isotopes and many secondary or qualifier isotopes for data confirmation.

Figure 1. Insects such as crickets have the potential to be sustainable, relatively low environmental impact, alternative sources of protein.

He KED mode is the only cell mode permitted in EAM 4.7 for single quadrupole ICP-MS. Reactive cell gas modes are not allowed, because of the risk of data errors due to cell-formed reaction product ions.

In this work, an Agilent 7850 ICP-MS was used to analyze four alternative proteins, supplied as finely ground powder:

- Cricket protein powder
- Reishi mushroom
- Almond flour
- Besan (chickpea) flour.

The samples were microwave digested in HNO_3 and HCl. HCl ensures the stability of critical trace elements including Hg. The standard He cell mode of the 7850 ensures accurate results for elements such as V, Cr, and As that could be overlapped by Cl-based polyatomic ions.

Certified Reference Materials (CRMs) are not yet available for alternative protein foods. But these novel foodstuffs have similar composition to conventional foods, so existing CRMs can be used for quality control. The results reported in reference 2 show accurate recovery of the EAM 4.7 elements in four representative food CRMs. Table 2 shows the measured concentrations for the EAM 4.7 analytes and the mineral elements in the four alternative protein samples measured in this work.

Table 1. Agilent 7850 ICP-MS concentrations for EAM 4.7 specified elements (in bold) and mineral elements in four alternative proteins. Results in original dried sample in µg/kg (ppb) except where indicated.
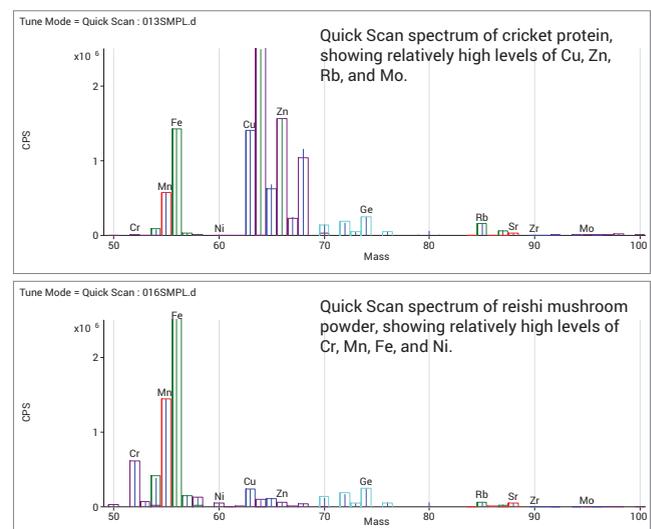
Element	Cricket Protein	Reishi Mushroom	Almond Meal	Besan Flour
Na (mg/kg)	3440	19.7	5.14	23
Mg (mg/kg)	1160	439	2880	1030
P (mg/kg)	9180	1030	5580	2490
K (mg/kg)	10100	1860	7190	8610
Ca (mg/kg)	1190	709	2370	522
Cr	**173**	**15500**	**58.2**	**61.3**
Mn (mg/kg)	36.6	82.4	25.3	14.7
Fe (mg/kg)	53.3	226	40.9	55.5
Ni	**214**	**2590**	**716**	**2210**
Cu (mg/kg)	29.1	4.71	10.8	8.34
Zn (mg/kg)	212	7.27	29.7	33
As	**36.4**	**86.5**	**23.2**	**7.76**
Se	**387**	**47.2**	**26.3**	**133**
Mo	**730**	**75.7**	**439**	**679**
Cd	**11.8**	**138**	**12.1**	**0.709**
Hg	**2.87**	**52.2**	**1.58**	**1.14**
Tl	**3.19**	**2.18**	**3.3**	**0.867**
Pb	**80.5**	**209**	**12.2**	**14.2**

The data in reference 2 demonstrates that Agilent ICP-MS systems provide accurate analysis of the EAM 4.7 regulated elements in a wide range of food sample matrices. The 7850 can also acquire He mode Quick Scan data for the full mass range with only an additional two seconds of acquisition time per sample.

Quick Scan data is processed using IntelliQuant to give semiquantitative results for practically every element, including those that were not present in the quantitative analysis calibrations. IntelliQuant results can also be presented in a periodic table "heat map" that gives an overview of the elemental content of each sample, as shown in Figure 2 for the cricket protein sample.
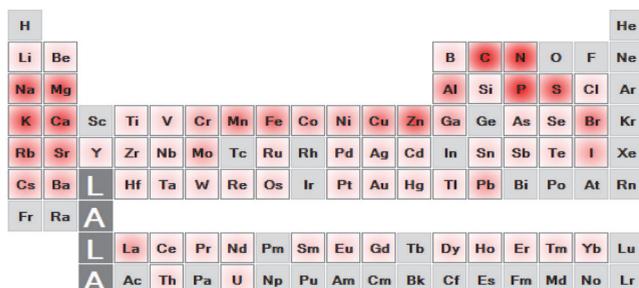
Figure 2. IntelliQuant periodic table heat map indicating relatively high levels (darker colors) of Cu and Zn in cricket protein (refer to Table 1).

Figure 3. Quick Scan data for cricket protein (top) and reishi mushroom (bottom). Quick Scan identifies unexpected elements and confirms identity using isotope template match. IntelliQuant gives semiquantitative concentrations without requiring element-specific standards.

Quick Scan collects data for every mass, so data is available for all isotopes of the measured elements. The presence of unexpected contaminants can be confirmed by comparing the measured Quick Scan data to the theoretical isotope abundance templates (Figure 3). For most elements, qualifier isotopes can be used to confirm the results from the primary or preferred isotope.

Conclusion

The Agilent 7850 ICP-MS uses He KED cell mode to provide accurate analysis of regulated elements defined in EAM 4.7. The 7850 can also perform Quick Scan elemental screening and IntelliQuant semiquantitative analysis to characterize the full elemental content of novel foods. The IntelliQuant results will enable food manufacturers and regulators to assess the safety of new food types.

References

1. Nelson, J. McCurdy, E., ICP-MS Analysis of Heavy Metals and Other Trace Elements in Alternative Proteins Per US FDA EAM 4.7, Agilent publication, 5994-5303EN

2. Nelson, J. *et al*, Determination of Heavy Metals and Trace Elements in Alternative Meats Per EAM 4.7 Method for ICP-MS. Agilent publication, 5994-5181EN

Using ICP-MS Trace Element Fingerprinting and MPP to Confirm the Region of Origin of High-Value Indian Teas

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Food fraud and elemental fingerprinting

The value of many food products – including wine, fruit juice, olive oil, honey, spices, and tea – is closely linked to the region or country of origin. The high value of these products makes them a target for fraudulent activities such as mislabeling, adulteration, or substitution, which can be difficult for regulators and consumers to identify.

India is the world's second largest producer of tea, after China (1). Among the well-known and popular varieties of Indian tea, Darjeeling, which is grown only in West Bengal, is among the most highly prized, which makes it a target for fraudsters (2).

Food producers and regulators use elemental analysis to help identify high-value foods. Many factors affect the elemental content of food, including elements derived from the soil, water, and local agricultural practices in the region of origin. These elements may provide a unique elemental "fingerprint" that can be used to confirm the origin of high-value products (3).

ICP-MS is the ideal analytical technique for elemental fingerprinting, as it has a unique combination of high speed, low detection limits, broad elemental coverage, and wide dynamic range. However, the use of ICP-MS for this analysis has previously been hampered by spectral interferences from the high and variable food matrices, which can cause errors for some trace elements.

Agilent ICP-MS instruments provide a solution to the analytical challenges of trace element fingerprinting food samples. The systems have an extremely robust (low CeO/Ce ratio) plasma that provides exceptional tolerance of the food matrices. This enables long analytical runs to be completed without requiring recalibration or excessive routine maintenance. Agilent ICP-MS systems also include an ORS[4] collision/reaction cell optimized for multi-element analysis using helium (He) cell gas and kinetic energy discrimination (KED). He KED provides universal


Figure 1. Indian tea is a high value product whose region of origin can be identified from its elemental fingerprint.

attenuation of common polyatomic ion overlaps, so results are more accurate, even in highly variable, high matrix samples, such as food digests.

The combination of a robust plasma and effective He KED provides more reliable results for a wider range of trace elements, giving the largest possible data set for discriminating between samples. Data processing is performed using Agilent Mass Profiler Professional (MPP) chemometrics software.

The ability of the Agilent 7850 ICP-MS to differentiate the region of origin of Indian tea varieties is illustrated in Figure 2. The plot shows a 3-D Principal Component Analysis (PCA) based on 18 "indicator" elements, identified from a total of 68 elements measured (4).
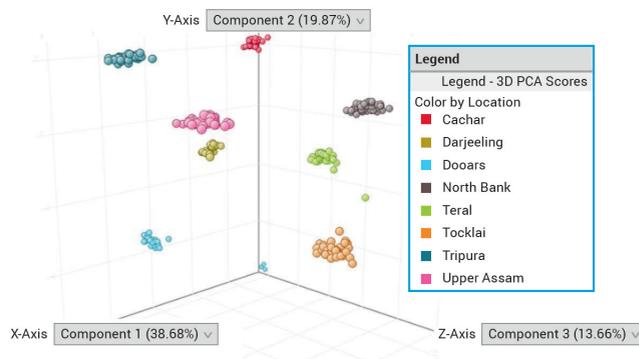
Figure 2. 3D Principal Component Analysis discriminates the region of origin of 150 tea samples based on differences in the concentrations of 18 indicator elements, measured using an Agilent 7850 ICP-MS.

Table 1. Actual and predicted geographical origin of 24 "unknown" tea samples, based on trace element profiles processed using MPP with SVM and LDA prediction models. All teas were correctly identified with a high degree of certainty (confidence measures close to 1).

Sample Name	Actual Location	SVM Prediction Model		LDA Prediction Model	
		Predicted Location	Confidence Measure	Predicted Location	Confidence Measure
Unknown C1	Cachar	Cachar	0.907	Cachar	0.986
Unknown C2	Cachar	Cachar	0.910	Cachar	0.967
Unknown C3	Cachar	Cachar	0.907	Cachar	0.977
Unknown D1	Dooars	Dooars	0.912	Dooars	0.976
Unknown D2	Dooars	Dooars	0.916	Dooars	0.966
Unknown D3	Dooars	Dooars	0.905	Dooars	0.964
Unknown Da1	Darjeeling	Darjeeling	0.886	Darjeeling	0.981
Unknown Da2	Darjeeling	Darjeeling	0.891	Darjeeling	0.979
Unknown Da3	Darjeeling	Darjeeling	0.906	Darjeeling	0.980
Unknown NB1	North Bank	North Bank	0.919	North Bank	0.978
Unknown NB2	North Bank	North Bank	0.921	North Bank	0.989
Unknown NB3	North Bank	North Bank	0.919	North Bank	0.989
Unknown T1	Tripura	Tripura	0.898	Tripura	0.985
Unknown T2	Tripura	Tripura	0.886	Tripura	0.977
Unknown T3	Tripura	Tripura	0.877	Tripura	0.940
Unknown Te1	Terai	Terai	0.902	Terai	0.980
Unknown Te2	Terai	Terai	0.905	Terai	0.986
Unknown Te3	Terai	Terai	0.911	Terai	0.983
Unknown To1	Tocklai	Tocklai	0.884	Tocklai	0.987
Unknown To2	Tocklai	Tocklai	0.887	Tocklai	0.981
Unknown To3	Tocklai	Tocklai	0.895	Tocklai	0.993
Unknown UA1	Upper Assam	Upper Assam	0.901	Upper Assam	0.985
Unknown UA2	Upper Assam	Upper Assam	0.913	Upper Assam	0.988
Unknown UA3	Upper Assam	Upper Assam	0.910	Upper Assam	0.985

The main variation in the elemental profiles was captured in the first three dimensions: PC1 (x-axis, mainly due to differences in Sr, Ba, and B), PC2 (y-axis, mainly Cs, La, and Rb), and PC3 (z-axis, mainly Mo, Ce, and Nd). Many of these elements were present at µg/kg (ppb) levels in the original tea samples, highlighting the benefit of the 7850 to provide accurate analysis at trace levels.

Two MPP class prediction models, support vector machine (SVM) and linear discriminant analysis (LDA), were trained using 126 of the digested tea samples. The models were then tested by taking the remaining 24 samples, randomly selected from eight different regions, and processing them as unknowns. The results in Table 1 show all samples were correctly identified with a high degree of certainty (confidence measures close to 1).

Conclusion

Agilent ICP-MS systems offer a unique and powerful ability to confirm the geographical original of high value products including foodstuffs such as tea. The 7850 includes a matrix tolerant (low CeO/Ce) plasma, low DLs, and unmatched He KED cell mode performance.

The combination allows a wider range of trace elements to be determined accurately at low levels in variable samples, providing a more complete and reliable data set for elemental fingerprinting using ICP-MS with MPP.

References

1. Food and Agriculture Organization of the United Nations, Commodities: Tea, accessed December 2022, Tea | FAO | Food and Agriculture Organization of the United Nations

2. Indian Chamber of Commerce, Sector: Tea, accessed December 2022, Tea - Indian Chamber of Commerce

3. Nelson, J., Hopfer, H., Authentication of Specialty Teas: An Application Note. *Food Qual. Safety,* **2018**, Specialty Tea Authentication: An Application Note (foodqualityandsafety.com)

4. Jain, V. *et.al.,* Authenticating Geographical Origin of Tea Using ICP-MS and Agilent Mass Profiler Professional Software, Agilent publication, 5994-4583EN

Battery Summit: Preparation and Analysis of Battery Samples

The rapid growth in the use of rechargeable batteries has led to increased interest in optimizing the analytical methods used throughout the industry, from testing raw materials to battery recycling. In December 2022, Agilent scientists presented a half day, 2.5-hour online symposium hosted by LCGC & Spectroscopy on the preparation and analysis of samples in the battery industry.

Yuhong Chen started the symposium with an overview of the principles of lithium-ion batteries (LIBs), the key components and materials used, and the role of analytical instrumentation in the battery life cycle.

Greg Gilleland presented method details and example results for elemental analysis of various battery components by ICP-OES. Jenny Nelson then talked about the benefits of ICP-MS for analysis of trace metals in LIB raw materials and recycled LIB components. Jenny also discussed the potential for triple quadrupole ICP-MS methods to determine even lower levels of trace element impurities in LIB materials.

Finally, Bartly Carlson and Shannon Coleman talked about leak detection for electric vehicle (EV) applications and the utilization of GC and GC/MSD for the analysis of swelling gas, carbonate solvents, and additives in LIBs.

You can now register for the on-demand summit here: Battery Summit: Preparation and Analysis of Battery Samples (chromatographyonline.com)

Latest Agilent ICP-MS publications

- **Application note:** Elemental and Particle Analysis of N-Methyl-2-Pyrrolidone (NMP) by ICP-QQQ, 5994-5365EN

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- **Application note:** Elemental Impurity Analysis of Lithium Ion Battery Anodes using Agilent ICP-MS, 5994-5475EN

- **Application note:** Accurate ICP-MS Analysis of Elemental Impurities in Electrolyte Used for Lithium-Ion Batteries, 5994-5363EN

- **Application brief:** ICP-MS Analysis of Trace Elements in LIB Cathode Materials, 5994-5509EN

- **Application brief:** Quantifying Metal Impurities in Li-Ion Battery Raw Materials by ICP-MS/MS, 5994-5341EN