Agilent

Trusted Answers

Agilent Solutions for Lithium-Ion Battery Industry

Lithium-Ion Battery Industry Is Thriving

High voltage, high specific energy, long cycle life, environmental friendliness, good energy density and power density, are some advantages of lithium-ion batteries in providing the best overall performance for power batteries. Li-ion batteries are widely used in fields such as consumer electronics (for mobile phones and laptops), mobility (for rail transit and new energy vehicles), and energy storage (small-scale power supply, uninterruptible power supply (UPS), communication base station, new energy), among others.

In recent years, there is a rapid growth of product output in the Li-ion battery industry. Coupled with the surge in the new energy vehicle market, power batteries have gradually become the main applications for lithium-ion batteries. In addition, there has been increased interest in the new energy and lithium-ion battery industries. Consequently, new requirements have been set for technological breakthroughs in lithium-ion batteries in terms of high safety, long life, and high energy density.

In the upstream and midstream of the lithium-ion battery industry chain, the quality control of raw materials and products requires instrumental analysis methods to test anode and cathode materials, electrolytes, separators, and other raw materials. In the midstream of the lithium-ion battery industry chain, a comprehensive physicochemical analysis on each part of the battery using instruments (e.g., atomic spectroscopy, molecular spectroscopy, chromatography and mass spectrometry) is also necessary for research and development on the product performance and safety. When recycling and reusing waste Li-ion batteries, a quantitative analysis on valuable metallic elements must be performed using instruments like atomic spectroscopy.

As a global leader in analytical technology, Agilent has extensive experience and data on testing Li-ion battery materials. We can help you realize your objectives, whether it is for raw material tests or scientific research.

Key Materials for Lithium-Ion Batteries

A lithium-ion battery works by repeated and reversible ingress and egress of lithium ions across anode and cathode materials to complete the conversion between chemical and electrical energies.

When charging, lithium ions run away from cathode materials, pass through electrolyte and separator, and enter into anode materials, while electrons are transferred, through external circuits, from cathode to anode materials. On the contrary, the discharge process is characterized by electrons transferring from anode to cathode materials to power external load equipment.

Four key materials for Li-ion batteries include anode and cathode materials, electrolytes, and separators

Cathode Materials

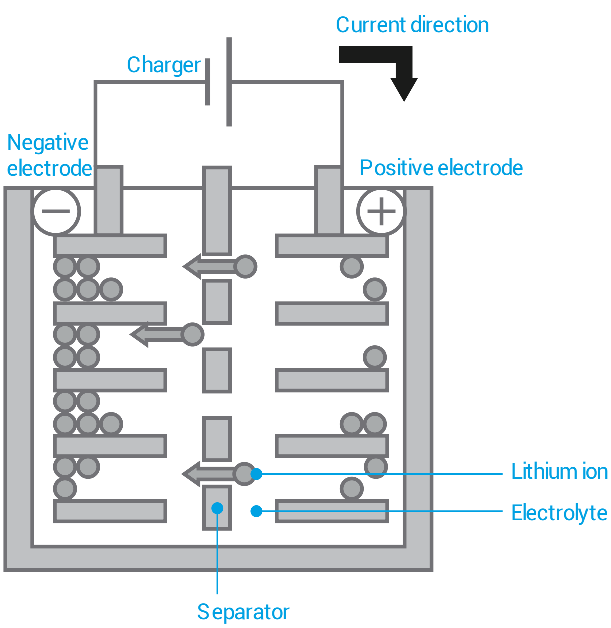
Cathode materials must be active materials with high oxidation-reduction potential, proneness to have chemical reactions, and structural stability, allowing batteries to achieve reversible and controllable energy storage and conversion. At present, the cathode materials commonly used in Li-ion batteries include a series of lithium-containing oxides, such as lithium cobaltate (LCO), lithium titanate (LTO), lithium iron phosphate (LFP), lithium manganese (LMO), and lithium nickel cobalt manganate (NCM; a lithium-ion ternary material).

The performance of cathode materials can affect Li-ion batteries mainly in terms of energy density, safety, and cycle life.

Anode Materials

In a Li-ion battery, materials allowing reversible ingress and egress of Lithium ions are used as anode materials. Compared to cathode materials, anode materials should have lower potential to be good energy carriers with relatively high stability. Many types of anode materials are used in lithium-ion batteries, and can be divided by chemical composition into metals (including alloys), inorganic non-metals (carbon, silicon and other materials) and metal oxides. Among them, the more mature technologies are those involving carbon-containing anode materials.

The performance of Li-ion anode materials is a main contributor to energy density of a Li-ion battery.



Schematic diagram of charging principle of Li-ion batteries.

Electrolyte

Electrolyte in a Li-ion battery is composed of high-purity organic solvents, electrolyte lithium salts, and additives. It is a non-aqueous medium through which lithium ions flow during charging and discharging of a lithium-ion battery. The performance of the electrolyte is critical for ensuring the safety of lithium-ion batteries.

Common electrolyte lithium salts include lithium hexafluorophosphate ($LiPF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), and lithium bisoxalate borate (LiBOB), among which $LiPF_6$ is now a more mature lithium salt product.

Solvents commonly used in Li-ion batteries include conventional carbonate solvents such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and propylene carbonate (PC), along with new organic solvents such as ethers and hydroxy acid esters.

As for electrolyte additives like vinylene carbonate (VC), fluoroethylene carbonate (FEC), vinyl ethylene carbonate (VEC) and biphenyl (BP), they can be functionally classified into SEI membrane optimizer, overcharge protection additive, flame retardant additive, additive to improve electrolyte conductivity, and additive to control water and acid content in electrolyte.

Separator

The separator in a Li-ion battery is a microporous structure film that separates active substances of positive and negative electrodes. A separator must possess good ion permeability to allow ions in the electrolyte to pass through freely, as well as insulation for safety purposes, to prevent any short circuit caused by contact between the two electrodes. Currently, separators with bulk applications in Li-ion batteries mainly include PP, PE and multilayer composite membranes.

The performance of the separator directly determines the interface structure of the battery, thereby affecting capacity, cycle performance, current density in charge and discharge, and other key electrical properties of the battery.

Common Analysis Items in the Lithium Battery Industry Chain

Lithium battery company raw material (upstream material) testing or lithium battery production management (cathode and anode materials, separator, electrolyte, etc.): including identification, and analyses on physicochemical properties, electrochemical performance, and chemical composition.

- Analysis of metal or magnetic impurities (AA, ICP-OES, and ICP-MS)
- Analysis of SO_4^{2-}, Cl^- and other anions, and non-metal elements such as Si (UV-Vis)
- Identification of raw materials such as electrolytes (FTIR)
- Assay of organics in graphite-based anode materials (GC/MS)
- Composition analysis and solvent component assay (GC and GC/MS) of electrolyte (including additives)

Research and development of Li-ion batteries: aims to improve key indicators of products, such as safety, cycle life, power density, and energy density

Gas composition analysis for battery swelling (GC and micro GC)

When evaluating the aging process of lithium-ion batteries, it is necessary to analyze the gas generated during battery degradation.

In a cell cycle, chemical reactions will be caused by the contact between the electrolyte and the positive/negative electrode, resulting in a swollen battery that poses a big safety risk. The composition of the battery swelling gas is commonly analyzed using gas chromatograph (GC).

Analysis of electrolyte and additives (GC and GC/MS)

The composition and content of ester compounds in the electrolyte are critical to the battery cycle performance.

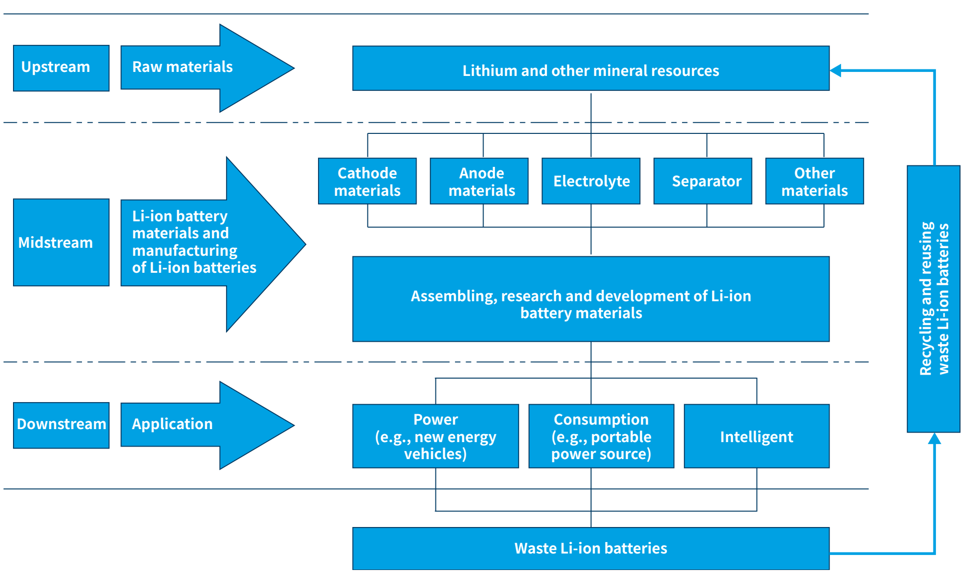
The organic electrolyte additive for Li-ion battery is low in consumption and cost, and yet able to improve performance in many aspects. To ensure a stable operating voltage and good performance of the battery at high and low temperatures, the content of each additive deserves more attention, which is usually analyzed by GC or GC/MS.

Analysis of unknown electrolyte components (GC/Q-TOF and LC/Q-TOF)

For unknown trace components produced in the circulation experiment, it is recommended to choose GC/Q-TOF or LC/Q-TOF for analysis.

Recycling of waste Li-ion batteries: Extract and recycle valuable metallic elements in waste Li-ion batteries

Analytical assay of valuable metallic elements (Ni, Co, Mn, Li, etc.) (AA and ICP-OES).



Agilent Atomic Spectroscopy in Lithium-Ion Battery Industry

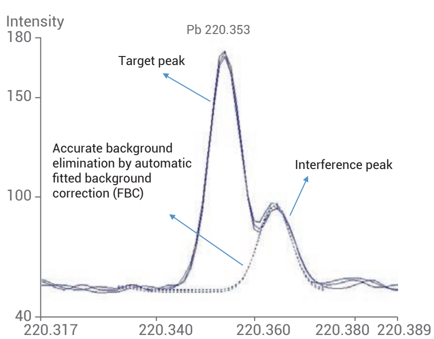
Robust matrix tolerance suited to extreme sample challenges

Industry assay demands

The composition of raw materials used in the production of Li-ion batteries need to be tested against quality standards. It is important to determine macro elements such as Li, Co, and Mn in the cathode and anode, the electrolyte, and other raw materials used in battery production. The impurities in the raw materials must also be strictly controlled since some contaminant elements can seriously affect the performance and lifespan of the battery.

A range of industry standard methods use ICP-OES or other analytical instrumentation with equivalent performance, to detect macro elements and trace impurity elements, and to analyze magnetic substances. Methods include GB/T 20252-2014 (Lithium Cobalt Oxide) and GB/T 24533-2019 (Graphite Negative Electrode Materials for Lithium Ion Battery). Other standard methods use AA, ICP-OES, or ICP-MS to detect Cd, Pb, Hg, Cr, and other restricted substances in batteries in accordance with IEC 62321 for determination of hazardous substances in electrotechnical products. These methods include GB/T 30835 2014 (Lithium Iron Phosphate-Carbon Composite Cathode Materials for Lithium Ion Battery), GB/T 24533-2019 (Graphite Negative Electrode Materials for Lithium Ion Battery), and GB/T 30836-2014 (Lithium Titanium Oxide and its Carbon Composite Anode Materials for Lithium Ion Battery).

5800/5900 ICP-OES



Background elimination using automatic fitted background correction (FBC).

Applications of ICP-OES

Challenges

The complex matrices of the cathode, anode, and electrolyte samples challenge the robustness of ICP-OES. The varied matrices also generate ionization, physical, or other interferences that need to be addressed.

Agilent solutions

– With its vertical torch and cooled cone interface (CCI), the Agilent 5800/5900 ICP-OES can handle complex matrices and overcome ionization interferences, ensuring robust, reliable, and stable assays regardless of the matrix.

– The VistaChip III CCD detector provides antiblooming protection on each pixel and provides high-speed continuous wavelength coverage. So, the 5800/5900 ICP-OES to achieve a high linear range for fast, simultaneous measurement of macro (Li, Co, Ni, etc.) and trace (Cu, Mg, Ba, etc.) elements in Li-ion battery materials.

– The background signals arising from the complex matrix of Li-ion battery materials can be automatically corrected using the Agilent fitted background correction (FBC) algorithm — a simple way to improve data-accuracy.

– Within the ICP Expert instrument control software, there are a series of smart ICP tools such as IntelliQuant, IntelliQuant Screening, Early Maintenance Feedback, Outlier Conditioning Formatting and Neb Alert all designed to identify problems before they happen, maximizing uptime and minimizing the number of samples you need to remeasure.

Typical application data

Macro and trace elements in a digestion solution of lithium nickel cobalt manganate (a ternary cathode material) were measured by ICP-OES. The sample and spike recovery results are provided in the following tables.

For the analysis of impurity elements in the electrolyte, lithium hexafluorophosphate, it was necessary to dilute the sample in an organic solvent. The sample and spike recovery results are provided in the following table. IntelliQunat Screening was used to assist with method development, particularly for wavelength selection as shown in figure below.

IntelliQunt Screening selects the best wavelengths for your analysis. Cu 324.754 nm received the best star rating due to Co interference on Cu 327.396 nm wavelength.

Analysis results of trace elements in lithium nickel cobalt manganate.

Trace element	Al	Ba	Be	Cu	Mg	Na	Sr
Wavelength	167.019 nm	493.408 nm	313.107 nm	324.754 nm	279.553 nm	589.592 nm	407.771 nm
Test result (mg/L)	0.004	0.001	0.001	0.0003	0.0823	0.277	0.0003
Spike amount (mg/L)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Spike result (mg/L)	0.097	0.099	0.09333	0.09933	0.17567	0.3703	0.09643
Recovery (%)	93	98	92	99	94	93	96

Analysis results of macro elements in lithium nickel cobalt manganate.

Macro element	Co	Li	Mn	Ni
Wavelength	236.379 nm	670.783 nm	280.108 nm	222.486 nm
Test result	19.7%	7.7%	18.6%	20.5%
RSD%, n = 6	0.21%	0.51%	0.27%	0.25%
Labeled content (%)	20 ± 2	7.6 ± 0.5	18.5 ± 2	20 ± 2

Analysis results of impurity elements in lithium hexafluorophosphate electrolyte.

Impurity element	Ca	Cd	Cr	Fe	Hg	K	Mg	Na	Pb
Wavelength	396.847 nm	226.502 nm	267.716 nm	259.940 nm	253.652 nm	766.491 nm	279.553 nm	588.995 nm	283.305 nm
Test result (mg/L)	0.0016	N.D.*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Spike amount (mg/L)	0.02	0.02	0.02	0.02	0.05	0.1	0.02	0.02	0.05
Spike result (mg/L)	0.021	0.019	0.020	0.018	0.056	0.104	0.019	0.020	0.045
Spike recovery (%)	98	97	98	91	111	104	97	98	90

** N.D.: Not detected*

7800 ICP-MS

7900 ICP-MS

Applications of ICP-MS

Challenges

Li-ion battery materials usually have a complex matrix and contain high levels of salts. Most ICP-MS cannot tolerate samples that contain more than 0.2%, total dissolved solids (TDS), so complex samples must be diluted before analysis, which can cause errors or contamination.

Agilent solutions

Agilent ICP-MS instruments use high/ultra-high matrix introduction (HMI/UHMI) aerosol dilution technology to increase ICP plasma robustness and allow % level TDS samples to be analyzed. This eliminates the need for conventional liquid dilution of complex samples, reducing sample preparation time and avoiding the risk of errors or contamination. Agilent HMI/UHMI enables routine analysis of samples that contain matrix levels up to 3% TDS (with HMI) or 25% TDS (with UHMI).

Typical application data

An Agilent 7900 ICP-MS was used to analyze three types of cathode material, lithium iron phosphate (LFP) and two ternary cathode materials (TCMs), lithium nickel cobalt manganate (NCM) and lithium nickel cobalt aluminate (NCA). The TDS content of the sample digests was 0.5–1%, so UHMI-Low was used. Other instrument operating settings were optimized automatically using the ICP-MS MassHunter autotune function. The sample results and excellent spike recoveries are shown in the following table.

7900 ICP-MS sample and spike recovery data for three types of cathode materials.

Sample	^{52}Cr [He]	^{63}Cu [He]	^{66}Zn [He]	^{75}As [He]	^{78}Se [He]	^{95}Mo [He]	^{111}Cd [He]	^{208}Pb [He]
NCA result (ng/mL)	0.368	0.299	2.243	2.532	1.341	N.D.	0.019	0.297
NCA+5 result (ng/mL)	5.259	5.36	6.613	7.018	5.886	4.94	4.999	5.464
Recovery (%)	97.8	101.2	87.4	89.7	90.9	98.8	99.6	103.3
NCM result (ng/mL)	2.186	1.123	1.512	3.81	0.626	0.164	0.551	0.355
NCM+5 result (ng/mL)	7.514	6.427	7.224	9.092	5.459	5.668	6.098	5.917
Recovery (%)	106.6	106.1	114.2	105.6	96.7	110.1	110.9	111.2
LFP result (ng/mL)	69.41	0.119	0.764	0.577	0.125	1.377	0.02	0.135
LFP+5 result (ng/mL)	74.133	4.782	5.975	5.478	4.47	6.531	5.461	5.461
Recovery (%)	94.5	93.3	104.2	98.0	86.9	103.1	108.8	106.5

Agilent Molecular Spectroscopy in Lithium-Ion Battery Industry

Efficiency. Accuracy. Robustness.

Agilent Cary 60 UV-Vis with Fiber Optics

Agilent Cary 630 FTIR

Assay Demands from Industry Chain

According to YS/T 582-2013 "Battery Grade Lithium Carbonate" and GB/T 26008-2020 "Battery Grade Lithium Hydorxide Monohydrate", it is required to detect substances like SO_4^{2-}, Cl^- and Si by spectrophotometry.

In GB/T 19282-2014 "Analytic Method For Lithium Hexafluorophosphate" and other relevant standards, it is required to perform a product identification assay by infrared spectroscopy (or equivalent).

Cary 60 UV-Vis

- A unique pulsed xenon flashlamp with an exceptionally long lifetime covers wavelengths in the ultraviolet-visible region, and can be used to directly replace 2 light sources (deuterium and tungsten lamps) of conventional UV-visible light spectrophotometer.
- Instant high energy output for more stable and accurate results.
- The measurement is not affected by the indoor light, so no need to close the sample chamber cover, which is more convenient for adding reagents or configuring different accessories.
- One-of-a-kind fiber optics eliminate the need to frequently change samples in the pool, delivering much higher productivity.

Cary 630 FTIR Spectrometer

- With compact design and ease of use, Cary 630 represents the world's smallest benchtop FTIR.
- Graphical working interface enables the simplest operation.
- Moisture and shock resistance, robustness, and operational reliability.
- Short optical path design to minimize interferences from water vapor and carbon dioxide in the air.
- Short time to results, with a detection speed of above 2 times that of a conventional system.

Agilent Micro GC in Lithium-Ion Battery Industry

Measure anytime, anywhere. Get results you need in seconds

Agilent 990 Micro GC

Assay Demands from Industry Chain

During recycling or storage of lithium-ion batteries, the SEI membrane may be decomposed to produce gases due to film formation and oxidation of the electrolyte components, overcharge and overdischarge of the battery, internal micro short circuit or others. Also, a battery swelling may be caused by gases from electrolysis at a high content of water, thereby posing high safety risks. Common gas-producing components include permanent gases (e.g., H_2, CO, and CO_2) and alkanes (e.g., CH_4, C_2H_4, and C_2H_6).

Agilent 990 Micro GC Field Case

Application of Micro GC

Agilent Solutions

Agilent recommends the Agilent 990 Micro GC for analysis of composition of battery swelling gases.

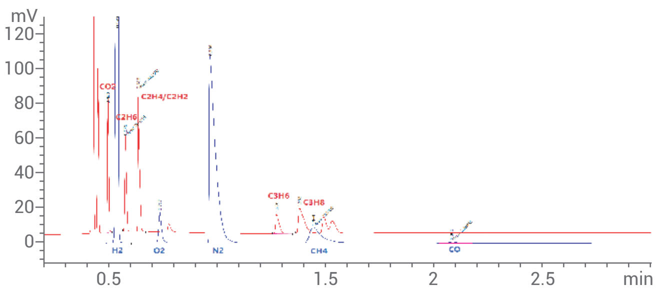
- The 990 Micro GC is an analytical instrumentation specially designed for gas composition analysis, and in standard version, it is combined with a micro-mechanical sampler and a highly sensitive TCD detector, which is suitable for the analysis of low-content components of battery swelling gases. Up to 4 independent analysis channels can be selected to simultaneously analyze different swelling gases. Each channel is a separate GC with pneumatics, sampler, column, and detector. The channel module is easy to configure, and ready to use.
- For lithium-ion battery swelling gases, 10–20 mL syringe for manual sampling is a common choice when using 990 micro GC, and the results can be obtained in only a few minutes after injection, delivering much higher efficiency in research, development, and test of Li-ion batteries.
- Compared to an ordinary benchtop GC, the 990 is more robust and compact, and also lower in consumption. This equipment is suitable for gas analysis in the laboratory, online and on-site, and can also be easily transferred between different test points. The optional portable field case, equipped with carrier gas supply and rechargeable batteries, increases the system’s flexibility even more.

Typical Application Data

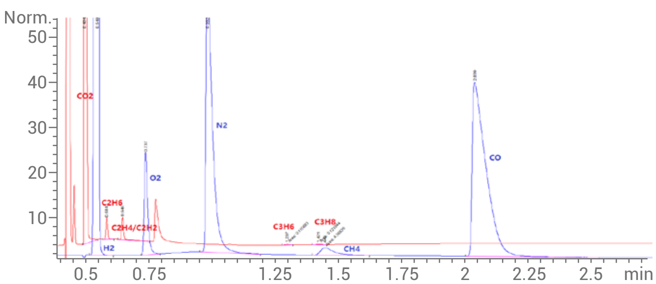
In this experiment, use the 990 micro GC to analyze the composition of Li-ion battery swelling gases, while selecting 2 channels, PPQ and MS5A. The table below provides the quantitative analysis results of the battery swelling gases; the following figures are the mixed standard gas spectrum and the swelling gas analysis spectrum for actual battery sample, respectively.

Quantitation results of Li-ion battery swelling gas

Ingredients	Peak Area	Concentration (%) (external standard method)	Concentration (%) (normalization)
H_2	716.3	23.6108	21.7778
O_2	15.68	4.2114	3.8844
N_2	78.42	21.1097	19.4708
CH_4	4.309	0.5974	0.5510
CO	105.2	41.6783	38.4425
CO_2	169.6	16.7355	15.4362
C_2H_4/C_2H_2	2.247	0.2355	0.2172
C_2H_6	2.437	0.2203	0.2032
C_3H_6	0.1158	0.0088	0.0081
C_3H_8	0.1252	0.0092	0.0085



Mixed standard gas spectrum



Swelling gas analysis spectrum for actual battery sample

Agilent GC and GC/MS in Lithium-Ion Battery Industry

Reliable, proven performance. A faster route to insight

Agilent 8890 GC

Agilent Intuvo 9000 GC and 5977B MS

Assay Demands from Industry Chain

– When testing and developing Li-ion electrolyte raw materials, GC/MS is a typical option for qualitative and quantitative analysis of Li-ion battery solvents (formulation ingredients) and additives.

– According to GB/T 24533-2019 "Graphite Negative Electrode Materials for Lithium Ion Battery" and other relevant standards for lithium-ion batteries, it is required to use GC/MS to detect organics such as polychlorinated biphenyls (PCBs), polybrominated biphenyl (PBBs), and acetone.

Application of GC and GC/MS

Agilent Solutions

Agilent recommends GC-FID or GC/MS for accurate and quantitative analysis, and GC/MS for qualitative analysis of formulation ingredients. The Agilent MassHunter toolkit effectively transforms data into scientific insights to help you quickly interpret data by complex sample matrix and obtain results.

– MassHunter Unknowns Analysis Software: Analyze spectra quickly and smartly. With a built-in automatic deconvolution software, the compound peaks can be purified faultlessly to improve the matching of detected compounds and the detection rate of low-content compounds. Also, the equipment will effectively eliminate the matrix interference in the background and enable automatic library matching during analysis of compounds in samples, allowing easy and intelligent acquisition of qualitative results of target substances in complex samples.

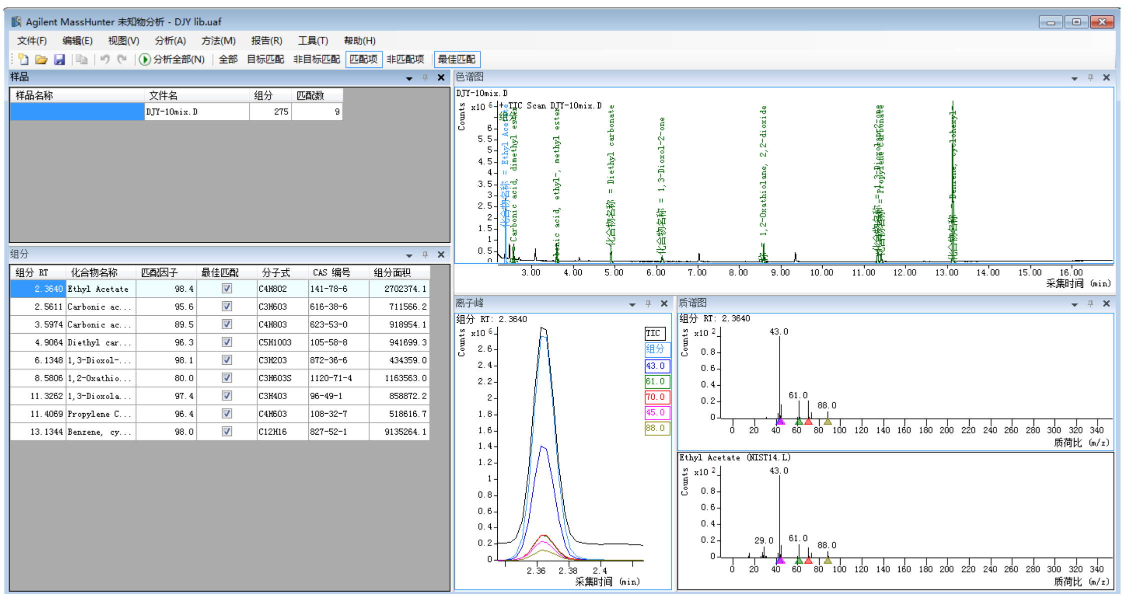
– MassHunter Library Editor: When it comes to electrolyte analysis, some compounds, due to advanced technologies or innovative compounds, are not included in the NIST library so that the corresponding qualitative analysis can not be managed by conventional ICP-MS. With the easy-to-use library editor in MassHunter software, the standard profiles and information for typical Li-ion battery electrolyte components on the market are now compiled into a special database for a later qualitative analysis of organics in the electrolyte.

Typical Application Data

In this experiment, the Agilent GC/MS platform are used in combination with MassHunter software to analyze 10 organic electrolyte components. The table and figure below respectively provide the selection of ion monitoring mode parameters and software operation interface during the analysis.

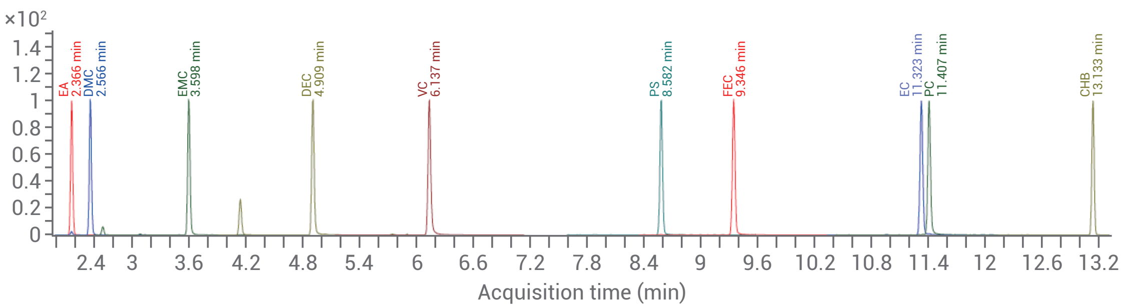
Selection of ion monitoring mode parameters for 10 organic electrolyte components

Compound name	Retention time	Quantifier	Qualifier 1	Qualifier 2
EA	2.329	88	70	61
DMC	2.526	90	62	59
EMC	3.601	77	45	59
DEC	4.928	91	45	63.31
VC	6.141	86	58	42.87
PS	8.593	92	58	65.57
FEC	9.363	62	106	43.29
EC	11.453	88	58	43.29
PC	11.503	87	102	57.43
CHB	13.151	160	117	104.91



MassHunter Unknowns Analysis Software: result interface of electrolyte sample analysis.

MassHunter Library Editor: information interface of electrolyte analysis database.



TIC chromatograms of 10 organic electrolyte components in "Scan" mode.

Agilent LC/Q-TOF and GC/Q-TOF in Lithium-Ion Battery Industry

High quality, high accuracy, and high resolution. Ideal tool to interpret unknowns

Agilent 6545 LC/Q-TOF

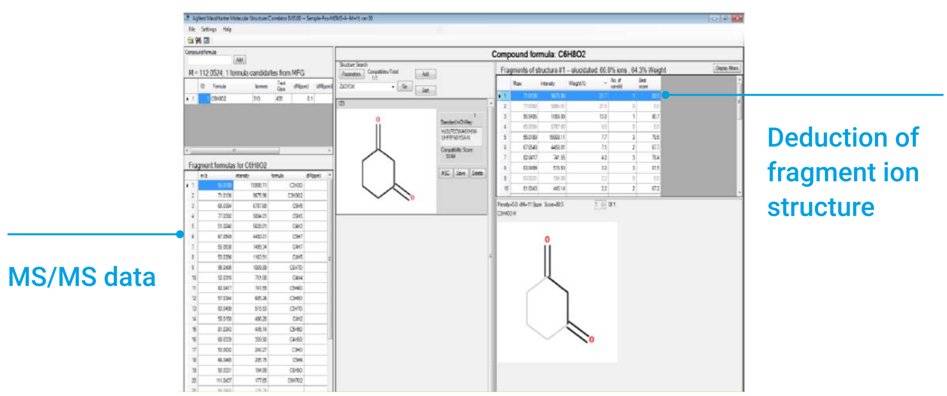
Agilent 7250 GC/Q-TOF

Assay Demands from Industry Chain

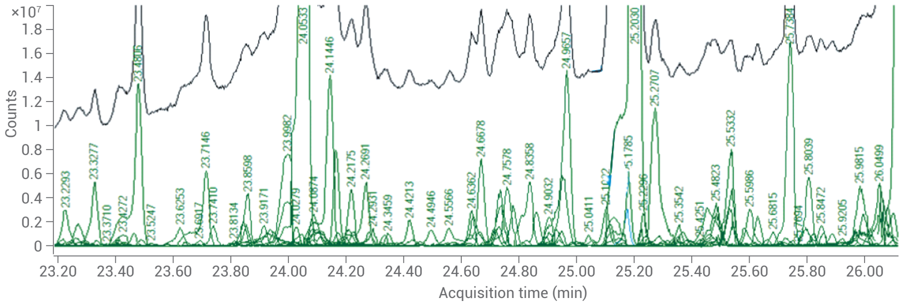
When developing a Li-ion battery, it is necessary to perform a qualitative analysis on unknown organics. For example, in the study of cycle performance, unknown electrolyte compounds introduced by a cell cycle is analyzed given that they may affect the battery's performance. Agilent recommends LC/Q-TOF or GC/Q-TOF for precise qualitative analysis of unknown compounds.

Application of LC/Q-TOF and GC/Q-TOF

– MassHunter MSC (MS/MS Structure Correlation; software for unknown structure derivation and analysis): For compounds with complex fragment ions yet without secondary mass spectrometry in the database, the software for unknown structure deduction and analysis can be used to infer the structure of unknown compounds.



– MassHunter MFE (molecular feature extraction) for molecular information extraction: A molecular feature extraction function (MFE) specially developed by LC/Q-TOF data features; can automatically and quickly sort out all compounds from the spectrum, and identify them by precise mass, isotope information, accurate secondary mass spectrometry and structure-assisted interpretation software.



– Mass Profiler Professional (MPP; statistical analysis software for MS data): Being compatible with GC/Q-TOF, LC /Q-TOF, ICP-MS and other mass spectrometry product data, the software can analyze all components in the sample, along with the significance of the difference using principal component analysis (PCA), unsupervised cluster analysis, analysis of variance, Venn diagram and other statistical analysis algorithms.

– Q-TOF Database and Library: Use a personal compound database (PCD) and a personal compound database and library (PCDL) for accurate mass search, providing the most comprehensive database and library in the industry.

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