JUNE 2025

TOSHVIN

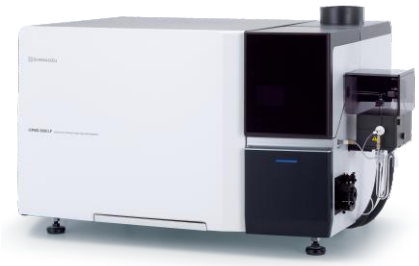
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NEWSLETTER FROM TOSHVIN ANALYTICAL



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ICPMS-2050



GCMS-QP2050

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Analysis of Trace Elements in Table Salt Using ICPMS-2050

Introduction

The Codex general standard for contaminants and toxins in food and feed (Codex) establishes requirements for levels of toxic metal elements in foods[1]. Inductively coupled plasma mass spectrometry (ICP-MS) systems can perform highly sensitive quantitative determination of multiple elements simultaneously, making them suited to the analysis of even trace amounts of toxic metal elements in foods.

Food samples are typically high-matrix samples that can often impact the clogging of torch or interfaces such as skimmer cone, non-spectral interference, and long-term stability in ICP-MS analysis.

This Application News uses the ICPMS-2050 (Fig. 1) to analyze table salt, a food with a particularly high matrix concentration. This analysis was performed using a mini-torch that features low argon gas consumption. The long-term stability and spike recovery were assessed based on the Food and Drug Administration (FDA) Elemental Analysis Manual (EAM) Section 4.7[2].

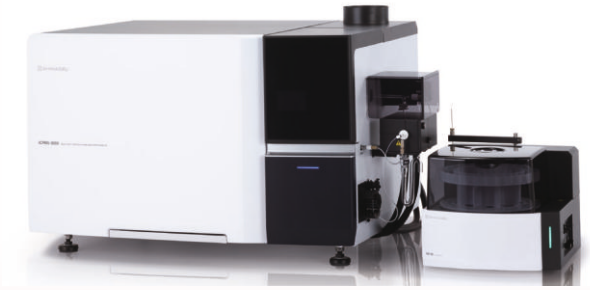


Fig. 1 ICPMS-2050 and AS-20 Equipment

Sample Preparation

The robustness of the ICPMS-2050 to sample matrix effects was evaluated using table salt, a food with a particularly high matrix concentration.

- Unspiked Sample

An unspiked sample was prepared by weighing out approx. 0.2 g of table salt, adding 2.5 mL of nitric acid, 0.25 mL of hydrochloric acid, and making the mixture up to 50 mL with pure water. The final concentration of table salt in the unspiked sample was approx. 0.4 %, the nitric acid concentration was 5 % v/v, and the hydrochloric acid concentration was 0.5 % v/v.

- Spiked Sample

A spiked sample was prepared by weighing out approx. 0.2 g of table salt, adding 2.5 mL of nitric acid, 0.25 mL of hydrochloric acid, adding commercially available single-element standard solutions of Al, Cr, Mn, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Hg, Tl, and Pb, then making the mixture up to 50 mL with pure water.

- Method Blank

A method blank was prepared by combining 2.5 mL of nitric acid with 0.25 mL of hydrochloric acid and making the mixture up to 50 mL with pure water.

Standard Samples

- Calibration Standards

Calibration standards were prepared by combining commercially available single-element standard solutions of Al, Cr, Mn, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Hg, Tl, and Pb and adding nitric acid and hydrochloric acid. The concentration of the target elements in each calibration standard is shown in Table 1.

- Internal Standard Solution

An internal standard solution was prepared by combining commercially available single-element standard solutions of Sc, Ge, Rh, Ir, and Bi and adding nitric acid to 5 % v/v and hydrochloric acid to 0.5 % v/v. The final concentration of Sc, Ge, Rh, Ir, and Bi in the internal standard solution was 2 mg/L.

- Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) Samples

ICV and CCV samples were prepared with the same target element concentrations as STD3 in Table 1.

- Continuing Calibration Blank (CCB) Sample

A CCB sample was prepared with the same target element concentrations as STD1 in Table 1.

Table 1 Target Element Concentrations in Calibration Standards

Elements	Calibration Standard (µg/L)			
	STD1	STD2	STD3	STD4
Cr, Ni, As, Se, Mo, Cd, Sn, Tl, Pb	0	1	5	10
Hg	0	0.1	0.5	1
Al, Mn, Cu, Zn,	0	10	50	100
Nitric acid	5 % v/v			
Hydrochloric acid	0.5 % v/v			

Equipment Configuration and Analytical Conditions

The configuration of the ICP-MS system is shown in Table 2. To reduce running costs, analysis was performed with a mini-torch that consumes less argon gas than a typical plasma torch. To reduce the labor involved in sample preparation, the internal standard sample was added online using an online internal standard kit.

The analytical conditions used are shown in Table 3. A complex investigation of conditions was avoided by using the analytical conditions from a preset method in LabSolutions™ ICPMS

Table 2 ICP-MS System Configuration

System:	ICPMS-2050
Nebulizer:	Nebulizer DC04
Chamber:	Cyclone Chamber
Torch:	Mini-Torch
Sampling Cone:	Nickel
Skimmer Cone:	Nickel
Autosampler:	AS-20
Internal Standard Elements	Online Internal Standard Kit (sample: internal standard = about 9 :1)

Table 3 Analytical Conditions

RF Power:	1.20 kW
Plasma Gas Flowrate:	9.0 L/min
Auxiliary Gas Flowrate:	1.10 L/min
Carrier Gas Flowrate:	0.35 L/min
Dilution Gas Flowrate:	0.55 L/min
Cell Gas:	He/H_2

Quantitative Analysis

A calibration curve was prepared using the calibration standards shown in Table 1. The unspiked sample, spiked sample, method blank, ICV sample, CCV sample, and CCB sample were quantitatively analyzed by this calibration curve.

Detection Limits (DLs)

Detection limits are shown in Table 4. The detection limits were calculated using the standard deviation (σ) of the calibration blank (STD1). Detection limits for the target elements in table salt were all at least one order of magnitude below the reference levels listed in the Codex.

Table 4 Detection Limits

Element	Cell Gas	Internal Standard Element	IDL (µg/L)	DL in Table Salt (mg/kg)	Codex Reference Level (mg/kg)
^{27}Al	H_2	^{45}Sc	0.09	0.02	–
^{52}Cr	He	^{74}Ge	0.1	0.03	–
^{55}Mn	He	^{74}Ge	0.07	0.02	–
^{60}Ni	He	^{74}Ge	0.09	0.02	–
^{65}Cu	He	^{74}Ge	0.09	0.02	–
^{66}Zn	He	^{74}Ge	0.2	0.04	–
^{75}As	He	^{74}Ge	0.08	0.02	0.5
^{78}Se	H_2	^{74}Ge	0.04	0.009	–
^{95}Mo	He	^{103}Rh	0.02	0.005	–
^{111}Cd	He	^{103}Rh	0.03	0.007	0.5
^{118}Sn	He	^{103}Rh	0.07	0.02	–
^{202}Hg	He	^{193}Ir	0.009	0.002	0.1
^{205}Tl	He	^{209}Bi	0.009	0.002	–
^{sum}Pb	He	^{209}Bi	0.008	0.002	1

IDL: Instrument detection limit (3σ × calibration curve gradient)
^{sum}Pb: Measured as the sum of ^{206}Pb, ^{207}Pb, and ^{208}Pb

Spike Recovery Test

A spike recovery test was performed to assess the effect of the sample matrix on analysis. The results are shown in Table 5. Good recovery of between 95 and 106 % was achieved for all elements, showing the sample matrix effect on the analysis remained allowably small. All recovery levels remained within 80 to 120 % as required by EAM Section 4.7.

Table 5 Spike Recovery Test

Element	Unspiked Sample (µg/L)	Spiked Conc. (µg/L)	Spiked Sample (µg/L)	Spike Recovery)(%
^{27}Al	N.D.	10	10.5	105
^{52}Cr	N.D.	1	0.99	99
^{55}Mn	5.47	10	15.5	100
^{60}Ni	N.D.	1	1.05	105
^{65}Cu	N.D.	10	9.68	97
^{66}Zn	N.D.	10	9.5	95
^{75}As	N.D.	1	1.05	105
^{78}Se	0.12	1	1.09	97
^{95}Mo	0.05	1	1.10	105
^{111}Cd	N.D.	1	0.96	96
^{118}Sn	N.D.	1	0.98	98
^{202}Hg	N.D.	0.1	0.106	106
^{205}Tl	N.D.	1	1.01	101
^{sum}Pb	0.741	1	1.77	103

Spike recovery (%) = (Spiked sample - Unspiked sample) / Spiked concentration × 100
N.D.: Below instrument detection limit (IDL)

Evaluation of Long-Term Stability

The long-term stability was assessed by the analysis for around 10 hours. The analytical sequence used was the calibration standards followed by the ICV sample, method blank, then test samples. The CCV sample and CCB sample were assayed every 10 test samples to confirm the validity of the calibration curve over the course of the evaluation. The analytical sequence is shown in Fig. 2.

Recovery rates from the ICV samples and CCV samples are plotted in Fig. 3. Recoveries from all ICV and CCV samples were within 90 and 110 % (red dashed lines) as required by EAM Section 4.7. All elements in the CCB sample were also assayed below the analytical solution quantification level (ASQL, 30σ × calibration curve slope[3].)

The change in signal intensity of the internal standard elements over the course of the evaluation is shown in Fig. 4, where the signal intensity of internal standard elements in STD1 is taken as 100 .% The change in signal intensity of the internal standard elements during the evaluation spanning around 10 hours remained within 60 to 120 % (red dashed lines) as required by EAM Section 4.7.

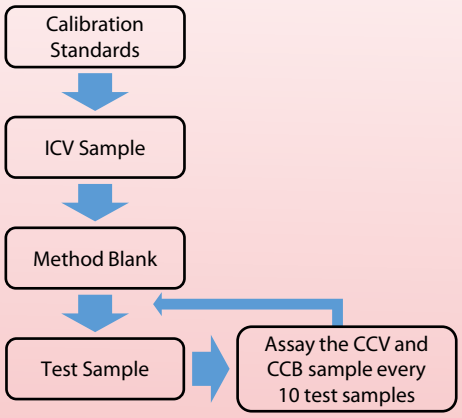


Fig. 2 Analytical Sequence

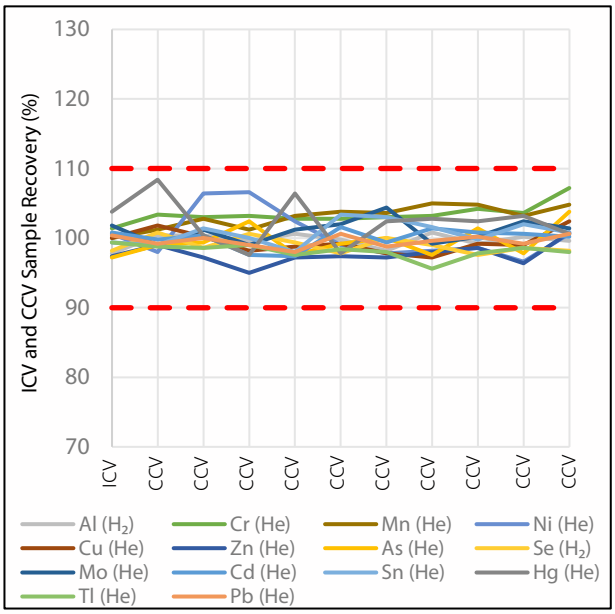


Fig. 3 ICV and CCV Sample Recovery

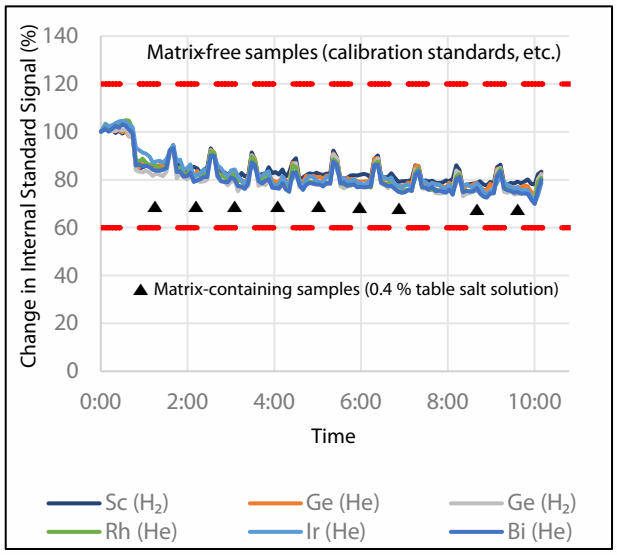


Fig. 4 Change in Signal of Internal Standard Elements during Approx. 10 Hours of Analysis

Conclusion

This Application News describes the use of the the ICPMS-2050 with a mini-torch to measure trace elements in table salt. The detection limits were sufficient to measure trace elements in table salt. Spike recovery testing showed good results even with high matrix concentration samples, confirming the accuracy of the analysis. The stability was also confirmed over the course of 10 hours of analysis.

The ICPMS-2050 performs highly sensitive, accurate, and stable analysis. The ICPMS-2050 can also reduce running costs by using a mini-torch that consumes less argon gas. Analytical conditions can also be entered from preset methods, simplifying analysis by avoiding a complex investigation of conditions.

<References>

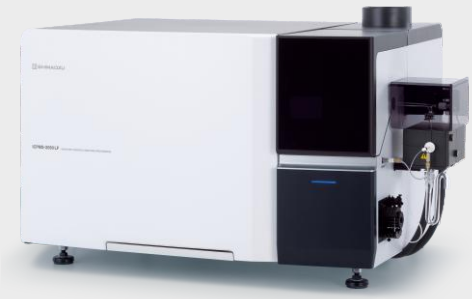
1) Codex general standard for contaminants and toxins in food and feed (CODEX STAN 193-1995)
2) U.S. Food and Drug Administration Elemental Analysis Manual 4.7 Inductively Coupled Plasma-Mass Spectrometric Determination of Arsenic, Cadmium, Chromium, Lead, Mercury, and Other Elements in Food Using Microwave Assisted Digestion, Version 1.2 (February 2020)
3) U.S. Food and Drug Administration Elemental Analysis Manual 3.2 Terminology, Version 3.0 (December 2021)

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Excellence in Science

ANALYTICAL INTELLIGENCE

An Era Without Compromise

- Deliver high sensitivity with low argon consumption using advanced mini-torch technology
- Eliminates spectral interferences with a redesigned collision/reaction cell
- Ensures long-term signal stability with patent pending charge stabilizer feature
- Proactive rinse with patent pending high gas purge mode for high throughput sample analysis
- Minimize carry over using Analytical Intelligence extended rinse feature
- Simplifies workflows with intelligent software, preset methods, and automation features.



ICPMS-2040/2050 Series

Elemental Analysis with Mercury Speciation in Honey Using LC-ICP-MS as per FSSAI Standard

Introduction

Honey is the natural sweet substance, produced by Honeybees from the nectar of plants. Honey has a superior nutritional value and contains a variety of minerals that are minor constituents. Elements such as Cu, Sn, and Zn are essential for normal metabolism in human and elements such as Pb, Cd, As and Hg are considered as toxic and harmful to human metabolism. Mercury (Hg) is considered as an element of concern for major public health by the World Health Organization (WHO)[1]. Methylmercury (CH_3Hg) is the most common and toxic organic form of mercury. The source of these toxic elements could be from air pollution, pesticides, industrial waste or natural disaster which goes from ground water to soil and then from plants nectar to Honeybees.

The potential for mercury contamination has become serious concern to human and environmental health. The contamination of mercury and its conversion to methylmercury is largely depending on the location in which it arrives. If the location is favorable, then the conversion of inorganic mercury to the significantly more toxic organic form of methylmercury happens.

The Food Safety and Standards Authority of India (FSSAI) has laid down limits of 1.0 mg/kg for total mercury and 0.25 mg/kg CH_3Hg in food products[2]. To meet these limits ICP-MS is widely used as an accurate and reliable technique for quantification.In the present study, one honey sample was analyzed using Shimadzu ICPMS-2040 for quantitation of total and inorganic mercury along with quantification of methyl mercury by coupling ICPMS-2040 to HPLC as a speciation technique.

Analysis of As, Cd, Cu, Hg, Pb, Sn and Zn

Sample preparation

The sample of Honey was purchased from local market. About 0.5 g of sample weighed accurately in PTFE vessels. 5 mL of suprapure nitric acid and 1 ml of suprapure hydrogen peroxide were added to it. The samples were then kept standing for 10 min to allow some pre-digestion.

The samples were digested in microwave digestion system using temperature program as per below Table 1. After the digestion was complete, the content was quantitatively transferred to 50 mL volumetric flask and diluted up to mark with distilled water. The samples were prepared in triplicates.

Table 1: Microwave digestion method

Ramp (Minute)	Temperature (°C)	Hold (Minute)
10	120	3
10	200	15

Preparation of additive recovery test solution

The samples were spiked at concentration levels of 10 % and 20 % of maximum permissible limits for recovery study. The maximum permissible limits are given in Table 2[2),3)]. The samples were prepared in triplicates.

Standard preparation

NIST traceable elemental standards were used for preparation of intermediate standard stock which were then further diluted to prepare final standard solution with concentrations as in Table 3.

Table 2. FSSAI maximum permissible limits in µg/g

Elements	FSSAI limits (µg/g)
Arsenic (As)	1.1
Cadmium (Cd)	1.5
Copper (Cu)	30
Mercury (Hg)	1
Lead (Pb)	2.5
Tin (Sn)	250
Zinc (Zn)	50
Methylmercury (CH_3Hg)	0.25

Table 3. The concentration of calibration standards in µg/L used in microwave digestion study

Element	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7
As	0.55	1.1	2.2	5.5	11	16.5	22
Cd	0.75	1.5	3.0	7.5	15	22.5	30
Cu	15	30	60	150	300	450	600
Hg	0.5	1	2	5	10	15	20
Pb	1.25	2.5	5	12.5	25	37.5	50
Sn	12.5	25	50	125	250	375	500
Zn	25	50	100	250	500	750	1,000

Instrument and Analytical Conditions

The Shimadzu ICPMS-2040 inductively coupled plasma mass spectrometer with auto sampler AS-20 is shown Figure 1. Analytical condition of ICPMS-2040 are shown in Table 4. In addition to providing high sensitivity, ICPMS-2040 is equipped with a collision system using helium gas, which reduces interferences from argon and chlorine significantly.

Table 4. Analytical conditions

Instrument	: ICPMS-2040
Auto sampler	: AS-20
RF Power	: 1.2 kW
Plasma gas flowrate	: 8 L/min
Auxiliary gas flowrate	: 1.1 L/min
Carrier gas flow	: 0.7 L/min
Nebulizer	: Nebulizer 10
Chamber	: Cyclone chamber (electronically cooled)
Plasma torch:	: Mini torch
Skimmer Cone/ Sampling Cone	: Copper / Nickel
Collision gas	: Helium



Fig.1 Inductively Coupled Plasma Mass Spectrometer ICPMS-2040 with Autosampler AS-20

Analysis

The calibration curve method was used for quantitative analysis of As, Cd, Cu, Hg, Pb, Sn and Zn. The internal standards used were Bi, Ce, Ge and Sc.

Results & Discussion

Correlation coefficient for As, Cd, Cu, Hg, Pb, Sn and Zn were more than 0.999. The analytical results along with instrument detection limit [IDL] are mentioned in Table 5. IDL's were determined using following procedure :The blank calibration curve sample solution was measured 10 times, and the concentration giving a signal 3 times blank standard deviation was calculated as the detection limit.

As there is no CRM available for honey matrix, to validate the developed method, spike recoveries were performed at 10 % and 20 % of the maximum permissible limit. The lowest calibration point corresponds to 5 % of the maximum permissible limit as per FSSAI guidelines. As per AOAC[4], the limit of quantification should be equal to or greater than lowest calibration point. In the present case, 10 % maximum permissible limit of FSSAI for individual elements can be considered as limit of quantification (LOQ). The LOQ values w.r.t sample are listed in Table 5. The recoveries for all elements at 10 % and 20 % maximum permissible limit concentration levels were between 90 to 120 %. The concentrations of all elements were below LOQ. The repeatability at concentration of 10 % and 20 % maximum permissible limit was good with RSD less than 3 %.

Table 5. LOQs established in the present work

Element	LOQ in ug/g
As	0.11
Cd	0.15
Cu	3
Hg	0.1
Pb	0.25
Sn	2.5
Zn	5

Table 6. The Results and Recovery test data at 10 % and 20 % of the maximum permissible limits (Average of 3 measurements)

Element	IDLs in (µg/L)	Sample Results in Honey (µg/g)	10 % Maximum permissible limit		20 % Maximum permissible limit	
			% Recovery	% RSD	% Recovery	% RSD
As	0.02	Below LOQ	105.9	2.3	102.0	0.8
Cd	0.003	Below LOQ	95.6	1.4	92.6	1.6
Cu	0.04	Below LOQ	117.9	0.4	111.1	2.0
Hg	0.02	Below LOQ	92.4	0.2	91.6	0.8
Pb	0.22	Below LOQ	109.1	1.0	105.0	2.1
Sn	0.17	Below LOQ	106.0	1.9	104.3	1.2
Zn	0.08	Below LOQ	109.0	1.4	106.5	2.2

* Note: In present work Spike recoveries for Sn were performed at 1% and 2% of FSSAI Maximum permissible limit.

Speciation Analysis of Mercury

Speciation analysis is defined by the International Union of Pure and Applied Chemistry (IUPAC) as an activity of identifying and measuring the quantities of one or more chemical species in a sample. In the present study, Inorganic mercury and methylmercury were analyzed using the LC-ICP-MS system as speciation analysis method.

Sample preparation

About 0.5 g of sample was accurately weighed into 10 mL volumetric flask (Dilution factor 20x). The samples were then made up to the volume by adding the mobile phase. The solutions were shaken using vortex. The samples were heated in water bath at 60°C for 2 h. The samples were cooled to room temperature. After cooling the samples were transferred to HPLC vial with filtration through 0.45 µm Nylon filter. The samples were prepared in six replicates.

The Standard preparation

All seven Intermediate standard stock solutions were prepared by mixing 1000 ppm stock solutions of inorganic mercury and methylmercury. These solution were then further diluted with 0.1%L- Cysteine (pH 2.5) to get final concentration as in Table 7.

Table 7. The concentration of calibration standards of methyl mercury & inorganic mercury

Calibration standard	Inorganic Mercury (µg/L)	Methyl Mercury (µg/L)
STD 1	0.1	0.1
STD 2	0.2	0.2
STD 3	0.5	0.5
STD 4	1.0	1.0
STD 5	2.0	2.0
STD 6	5.0	5.0
STD 7	10.0	10.0

Preparation of additive recovery test solution

The samples were spiked at concentration levels of 0.2 µg/L and 0.5 µg/L for recovery study. The samples were prepared in six replicates

Instrument and Analytical Conditions

ICPMS-2040 and LC-20Ai were used as LC-ICP-MS systems (Shown in Figure 2). In LC-ICP-MS systems using inert LC and ICP-MS, LabSolutions ICPMS Time Resolved Measurement (TRM) software can perform LC control, ICP-MS measurements and chromatographic data analysis. The analysis conditions for each instrument are shown in Tables 8 and 9.

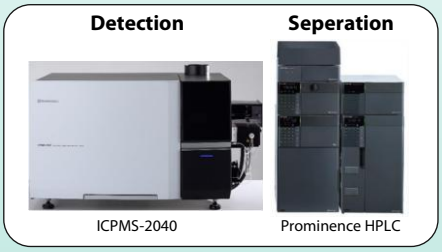


Fig. 2 Hyphenation of ICPMS-2040 (Left) with Inert LC-20Ai (right) using single LabSolution ICPMS software

Table 8. Chromatographic conditions

Instrument	: LC-20Ai inert LC
Column	: Synergi Hydro RP 150 x 4.6 mm, 4 µm.
Mobile phase	: 0.1 % L-Cysteine pH adjusted to 2.5
Flow rate	: 1.2 mL/min
Columntemp .	: 25 °C
Injection volume	: 100 µL
Run time	: 5 min

Table 9. Analytical conditions of ICP-MS

Instrument	: ICPMS-2040
RF Power	: 1.2 kW
Plasma gas flowrate	: 8 L/min
Auxiliary gas flowrate	: 1.1 L/min
Carrier gas flow	: 0.7 L/min
Chamber	: Cyclone chamber (electronically cooled)
Plasma torch:	: Mini torch
Collision gas	: Helium

Analysis

Inorganic mercury and methylmercury in the sample solution were quantitatively analyzed by the calibration curve method using the LC-ICP-MS system. In addition, for validation of analytical values, samples for additive recovery tests were used. Table 8 shows the analysis conditions for the chromograph, and Table 9 shows the analysis conditions for ICP-MS

Results & Discussion

Chromatograms of inorganic mercury and methylmercury are shown in Figure 3. In this speciation analysis, one sample can be measured within five minutes, and the peaks of each species are well separated.

Figure 4 shows the calibration curve for each species of mercury. The calibration curve showed a correlation coefficient of more than 0.999.. As per AOAC[4], the limit of quantification should be equal to or greater than lowest calibration point. In the present work, 0.1 µg/L was the lowest calibration point. To establish LOQ, the samples were spiked at the concentration levels of 0.2 µg/L and 0.5 µg/L.

The results obtained along with LOQ are shown in Table 10. The 0.2 µg/L (4 µg/kg in honey sample)can be considered as limit of quantification (LOQ). The concentrations of both the species was below LOQ. The % recovery at 0.2 µg/L and 0.5 µg/L was between 90 to 120%, with good repeatability. The % RSD obtained for six measurements was less than 5. IDL's mentioned in Table 10 were determined using following procedure :The blank calibration curve sample solution was measured 10 times, and the concentration giving a signal 3 times blank standard deviation was calculated as the detection limit. The integration of blank signal was performed manually.

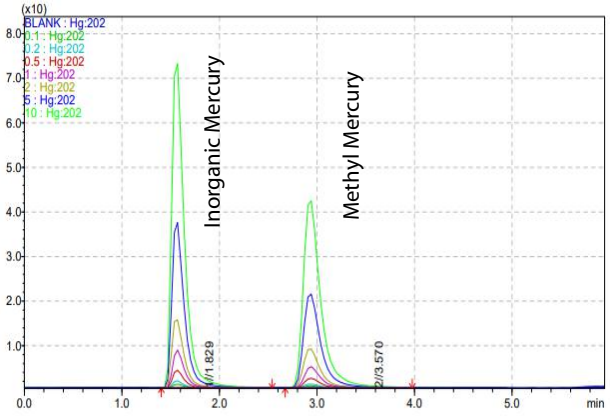


Fig. 3 Chromatogram obtained in the present study

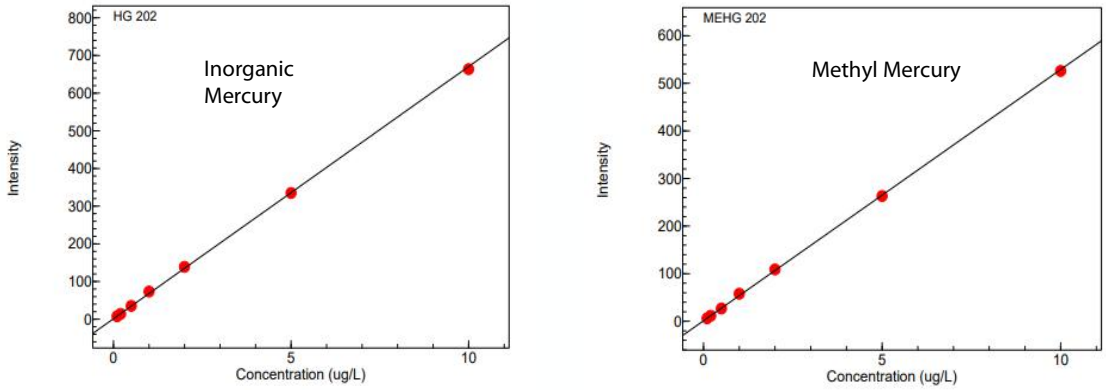


Fig. 4 Calibration curves of Inorganic mercury and Methyl mercury obtained in the present study

Table 10. Sample results and recovery data at 0.2 µg/L and 0.5 µg/L for inorganic mercury and methylmercury (Average of 6 measurements)

Analyte	IDL in (µg/L)	LOQ (µg/kg)	Sample Results in Honey (µg/kg)	Recovery at 0.2 µg/L		Recovery at 0.5 µg/L	
				% Recovery	% RSD	% Recovery	% RSD
Inorganic mercury	0.025	4	Below LOQ	94.3	3.9	96.4	2.3
Methyl mercury	0.016	4	Below LOQ	107.3	3.4	109.6	4.9

Conclusion

The present work demonstrates the suitability of the HPLC-ICP-MS method for the quantification of inorganic mercury and methylmercury in honey, in accordance with FSSAI regulations. The inorganic and methylmercury forms of Hg were measured accurately at low-ppb concentrations in honey sample using a Shimadzu Inert HPLC LC-20Ai coupled to a Shimadzu ICPMS-2040. The separation of both species was complete in less than five minutes.LabSolutions TRM software can perform LC and ICP-MS measurements. ICPMS-2040 enables quantitative analysis of elements essential for normal metabolism such as Cu, Sn and Zn and toxic trace elements such as Pb, Cd, As and Hg in honey. Excellent detection limits were obtained using Shimadzu ICPMS-2040 with unique mini-torch technology which uses lowest argon flow rates as compared to any other conventional ICPMS.

Reference

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2. Food Safety and Standards Authority of India, Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011

3. FSSAI, Food Safety and Standards (Contaminants, Toxins and Residues), Regulations, 2006

4. Briscoe M., Determination of Heavy Metals in Food by Inductively Coupled Plasma-Mass Spectrometry: First Action 2015.01, J.AOAC Int. 2015, 98 (4), 1113-1120. 98(4), 1113–1120

Note

This application is based on ICPMS-2040, but similar analysis can be performed with ICPMS-2040/2050.

In this case, the ICP-MS analysis conditions shown in Table 9 should be suitable for ICPMS-2040/2050

Analysis of Carbonate Esters, Additives, and Phosphate Esters in Lithium-Ion Battery Electrolyte Using GCMS-QP2050

Introduction

In recent years, lithium-ion batteries have rapidly gained traction in fields, including electric vehicles and portable electronic devices, owing to high energy density and long lifespan. This widespread adoption is largely driven by increasing demand for sustainable energy solutions and advancements in technology. The performance of lithium-ion batteries is significantly influenced by the composition and purity of carbonate esters and additives in the electrolyte, as well as by impurities introduced during manufacturing or formed during storage. Therefore, qualitative and quantitative analysis of these components is critically important.

In a previous publication[1], quantitative analysis of carbonate esters and additives in electrolytes was demonstrated using the Brevis™ GC-2050 + FID. In this report, equivalent quantitative analyses were conducted using the GCMS-QP2050 (Fig. 1), and additional qualitative examinations of impurities were performed. GCMS-QP2050, with its high analytical performance and space-saving design, contributes to highly precise analyses. Furthermore, combining it with AOC™-30i auto-injector delivers enhanced accuracy, improved analytical stability, and increased productivity.



Fig. 1 AOC™-30i+GCMS-QP2050

Analysis Conditions

The analytical conditions are shown in Table 1. For liquid injection, the Shimadzu Xtra Life Microsyringe (P/N 221-35400-01), equipped with a titanium alloy plunger and optimized for long-term analysis, was utilized.

Table 1 Analysis Condition

GC-MS Model	: GCMS-QP2050
Autoinjector	: AOC-30i
[GC]	
Collumn	: SH-I-5MS (P/N 221-75940-30) (30 m × 0.25 mm I.D., 0.25 µm)
Inj. Temp.	: 250 ˚C
Inj. Mode	: Split
Split Ratio	: 50
Carrier Gas	: He, constant linear velocity (40 cm/sec)
Collumn Temp.	: 40 ˚C (3 min) → 10 ˚C/min → 160 ˚C (5 min)
[MS]	
Ion Source Temp.	: 200 ˚C
Interface Temp.	: 230 ˚C
Pumping speed	: 255 L/s
Acquisition Mode	: SIM
SIM monitoring m/z	: Refer to Table 2

Chromatogram of Mixed Standard Solution of Eight Components

A mixed standard solution comprising eight carbonate esters and additives commonly utilized in electrolytes was prepared. The TIC chromatogram obtained from a 100 mg/L solution analyzed under the conditions of Table 1 is showed in Fig. 2.

Table 2 Eight target carbonate esters and additives with the selected ions for SIM

No.	Compound	Abb.	Quantitative ion (m/z)	Qualitative ion (m/z)
1	Dimethyl carbonate	DMC	45	59, 62
2	Ethyl methyl carbonate	EMC	45	59, 77
3	Vinylene carbonate	VC	86	42, 58
4	Diethyl carbonate	DEC	45	63, 91
5	Fluoroethylene carbonate	FEC	62	43, 47
6	Ethylene carbonate	EC	43	44, 88
7	Propylene carbonate	PC	57	43, 87
8	1,3-Propanesultone	PS	58	41, 57

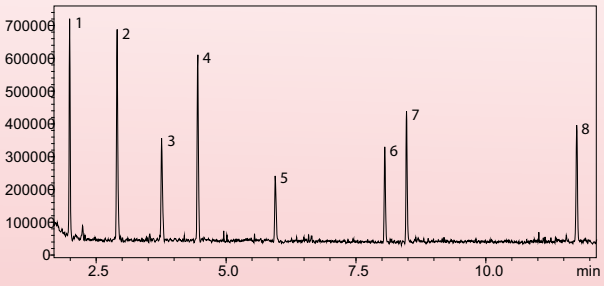


Fig. 2 Chromatogram of mixed standard sample of eight compounds (100 mg/L)

Calibration Curve and Repeatability of Mixed Standard Solution of Eight Components

Eight component mixed standard solutions were prepared in dichloromethane at six concentration levels(10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, and 500 mg/L) for the purpose of constructing calibration curves and assessing reproducibility. The calibration curves for each compound are depicted in Fig. 3, demonstrating excellent linearity (R^2 > 0.999). In addition, the repeatability(% RSD) of peak area values, determined from five consecutive injections of the 10 mg/L standard solution (Table 3). All compounds exhibited favorable repeatability.

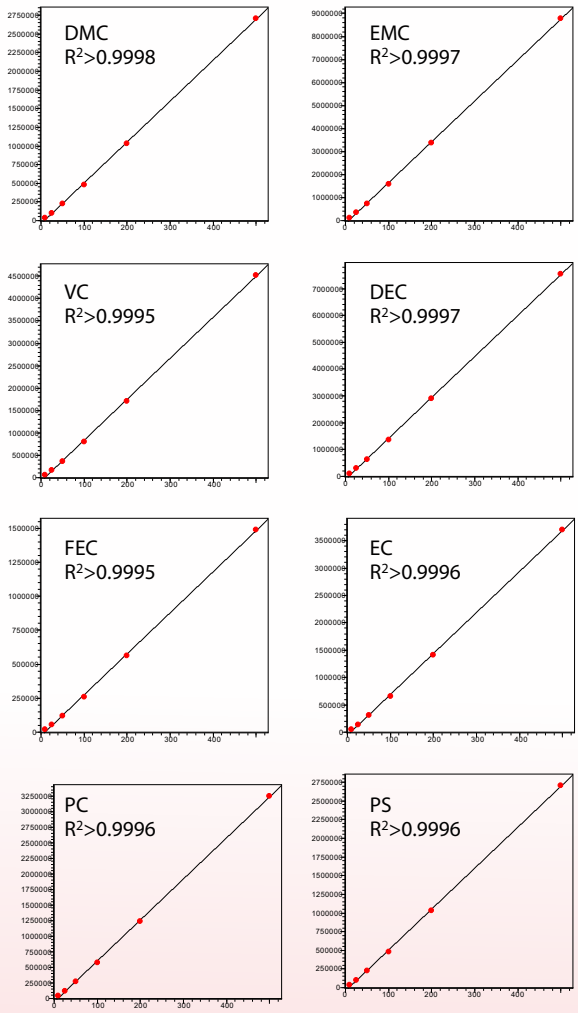


Fig. 3 Calibration Curves of eight compounds

Table 3 Peak area repeatability (%RSD) of 10 mg/L standard solution (n = 5)

Compound (Abb.)	%RSD
DMC	6.3
EMC	6.2
VC	6.4
DEC	6.2
FEC	6.4
EC	5.7
PC	6.0
PS	5.9

Quantitative Analysis of Actual Electrolyte samples

Based on the calibration curves described above, four types of commercially available lithium-ion battery electrolytes, each differing in electrolyte composition and contained carbonate esters, were subjected to quantitative analysis (Table 4).

In this study, the samples were diluted 1,000-fold with dichloromethane prior to analysis. If the samples are analyzed in the undiluted state, the effect of electrolyte precipitation will be excessive, and thus reducing analytical efficiency. In addition, such precipitation may lead to device failures.

Sample handling was conducted in a glove box because there is a risk of hazardous reactions between atmospheric moisture and the Li-based electrolyte.

The chromatograms for each sample are shown in Fig. 4, and the quantitative values for the carbonate esters in each undiluted sample are summarized in Table 5. Notably, for the samples containing $LiPF_6$, peaks suspected to be impurities were detected in addition to those of the included carbonate esters (Fig. 4, arrows).

Table 4 The characteristic of four actual samples

	Electolyte	Carbonate esters
Sample A	LiFSI	DMC、EMC、EC
Sample B	LiFSI	DMC、DEC、EC
Sample C	$LiPF_6$	DMC、EMC、EC
Sample D	$LiPF_6$	DMC、DEC、EC

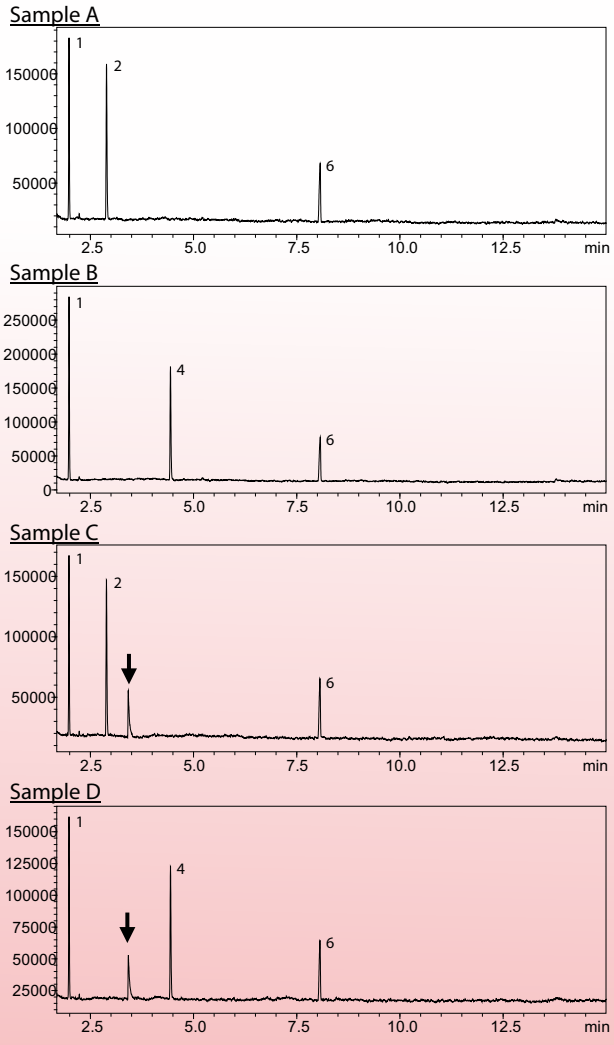


Fig. 4 Chromatograms of four samples

Table 5 Quantitative values of four samples (mg/L)

No.	Compound	Sample A	Sample B	Sample C	Sample D
1	DMC	507	496	527	551
2	EMC	450	—	470	—
3	VC	—	—	—	—
4	DEC	—	438	—	486
5	FEC	—	—	—	—
6	EC	560	539	585	576
7	PC	—	—	—	—
8	PS	—	—	—	—

Qualitative Analysis of Impurities in $LiPF_6$-Based Electrolytes using Low Ionization Energy (LEI)

Qualitative analysis was performed on an unknown component in the $LiPF_6$-based electrolyte indicated by the arrows in Fig. 4 using simultaneous Scan/SIM analysis (FASST) (Scan Event Time : 0.3 s, Scan m/z Range :35–500 .)

Use of $LiPF_6$ as an electrolyte can lead to the formation of volatile phosphate esters, particularly at elevated operating voltages or over extended run times .Dimethyl fluorophosphate (DMFP), which has a molecular ion at m/z 128 and a principal fragment ion at m/z 98 ,is one of the phosphate esters[2].

Although DMFP is not registered in the mass spectral library used in this study, qualitative analysis was conducted using information on the molecular ion, which is critically important for identification . However, in the mass spectrum acquired in Scan mode, the signal intensity for the molecular ion at m/z 128 was weaker than that of the fragment ions (upper part of Fig. 6, arrow).

To enhance detection of the molecular ion peak, a low-electron-ionization-energy (LEI) technique was employed . Specifically, the ionization voltage was lowered from 70 V (the standard EI setting) to 14 V. Under these conditions, the signal intensity for the molecular ion at m/z 128 increased by approximately four-fold (Fig. 6, bottom, arrow).

Based on prior investigations, the four-fold increase in the m/z 128 molecular ion signal in LEI, and the absence of this peak in the LiFSI-based electrolyte, the impurity was inferred to be DMFP . Notably, under standard qualitative workflows, mass spectral library searches and comparison of retention times against reference standards afford straightforward identification of unknown peaks.

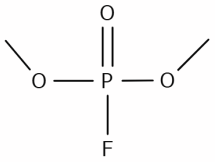


Fig. 5 Dimethyl fluorophosphate (DMFP)

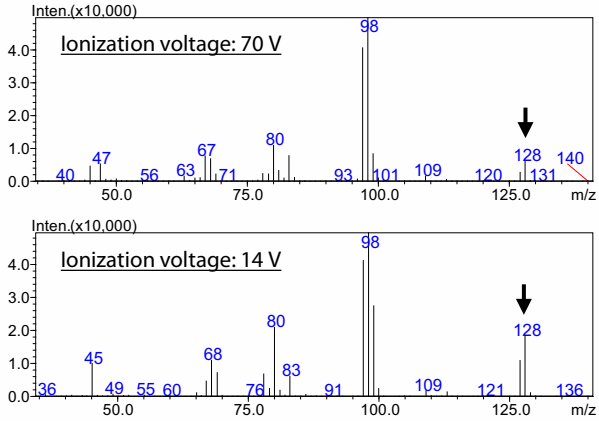


Fig. 6 Mass spectra of DMFP

Conclusion

In this study, eight commonly used carbonate esters and additives in lithium-ion battery electrolytes were quantified using the GCMS-QP2050 . The standard mixture exhibited chromatographic separation, and the calibration curve indicated excellent linearity . Analysis of four commercial electrolyte samples detected and quantified multiple carbonate esters.

Additionally, impurities were detected in these samples . By applying low-electron-ionization (LEI) to strengthen the molecular ion signal, the impurity was identified as DMFP.

<Related Applications>

1) Analysis of Carbonic Esters and Additives in Lithium Ion Battery Electrolytes, Application News No.01-00708

<References>

2) Weber et al., Ion and gas chromatography mass investigations of organophosphates in lithium ion battery electrolytes by electrochemical aging at elevated cathode potentials. Journal of Power Sources. 306, 193-199 (2016).

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Simultaneous Analysis of 19 Organic Solvents and Additives in Lithium-Ion Battery Electrolytes Using GC-MS

■ Introduction

Lithium-ion batteries (LIBs) are eco-friendly, rechargeable energy storage devices that provide a sustainable alternative to fossil fuels .They are widely used to power electric vehicles and store energy generated from renewable sources, thereby reducing dependence on fossil fuels and lowering greenhouse gas emissions . As a result, LIBs play a essential role in the transition toward low-carbon and sustainable energy systems.

The electrolytes in LIB consists of a lithium salt dissolved in a mixture of organic solvents and formulated with various functional additives .The organic solvents act as the vehicle for lithium-ion transport between electrodes, while the additives improve electrolytes stability, safety, and overall performance by enabling stable operation under various conditions . Both organic solvents and additives play an essential roles in the function and performance of LIBs .

Accurate control of electrolytes composition is critical, as even minor impurities in the solvents or additives can result in significant safety risks and degradation of battery performance . Therefore, the analysis of electrolytes composition and its operational degradation products is essential for ensuring the safety, stability, and quality of LIBs throughout their development and production. In a previous Application News, the analysis of seven compounds used as organic solvents and additives in LIB electrolytes using GC-FID was proposed.[1]

In this study, an analytical method of 19 organic solvents and additives commonly used in LIBs electrolytes was developed . The analysis was carried out using the Shimadzu Nexis™ GC-2030 gas chromatograph coupled with the QP2020NX single quadrupole mass spectrometer . The developed method was successfully applied to commercial LIB electrolyte sample.



Figure 1. Nexis GC-2030 + QP2020 NX

■ Materials & Method

Analytes and Analytical Conditions

In this study, 19 target compounds mainly used as organic solvents and additives in the LIB electrolytes were selected and then analyzed for simultaneous analysis using SHIMADZU GC-2030 + QP2020NX (Figure 1).

All 19 standard compounds were obtained from TCI Chemical (Tokyo, Japan) and dichloromethane (DCM) was purchased from Tedia (Fairfield, OH, USA) . Detailed analytical conditions of the instrument are shown in Table 1 and 2.

Table 1. Analytical method of GC-MS

GC System	**Nexis GC-2030**
Carrier Gas	: He (99.999 %)
Flow Control Mode	: Constant linear velocity
Liner Velocity	: 36 cm/s
Injector Temp.	: 250 °C
Injection Mode	: Split (10:1)
Column Flow	: 1.0 mL/min
Analytical Column	: SH-1701 (30 m x 0.25 mm ID, 0.25 µm)
Column Temp.	: 35 °C (3 min) → 10 °C/min → 240 °C (5 min)
MS System	**QP2020NX**
Ionization Method	: EI Mode
Ion source Temp.	: 250 °C
Interface Temp.	: 300 °C
Acquisition Mode	: SIM mode (refer to Table 2)

Table 2. The retention times and the selected ions used for quantitative and qualitative analysis of the 19 target compounds.

No.	Compounds	Abbreviation	Cas No.	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)
1	Ethyl acetate	EA	141-78-6	2.855	43	29, 45
2	Tris(trimethylsilyl) Phosphite	TMSP	1795-31-9	2.865	147	73, 131
3	Methyl propionate	MP	554-12-1	3.08	57	59, 88
4	Dimethyl carbonate	DMC	616-38-6	3.147	45	31, 59
5	Fluorobenzene	FB	462-06-6	3.608	96	70, 50
6	Ethyl propionate	EP	105-37-3	4.486	57	29, 74
7	Ethyl methyl carbonate	EMC	623-53-0	4.677	45	29, 77
8	Diethyl carbonate	DEC	105-58-8	6.36	45	31, 91
9	n-Propyl propionate	PP	106-36-5	6.526	57	75, 43
10	Vinylene carbonate	VC	872-36-6	7.694	86	29, 42
11	Fluoroethylene carbonate	FEC	114435-02-8	11.045	29	62, 33
12	1,1–dimethylpropylbenzene(tert-Amylbenzene)	TAB	2049-95-8	11.428	119	91, 41
13	Ethylene carbonate	EC	96-49-1	13.106	29	43, 88
14	Propylene Carbonate	PC	108-32-7	13.191	57	43, 30
15	Vinyl ethylene carbonate	VEC	4427-96-7	14.082	42	39, 40
16	Succinonitrile	SN	110-61-2	14.198	53	40, 79
17	Ethylene sulfate (1,3,2-Dioxathiolan-2,2-oxide)	DTD	1072-53-3	15.309	31	30, 29
18	1,3-Propanesultone	PS	1120-71-4	16.652	58	29, 57
19	1,4-Dicyanobutane(Adiponitrile)	ADN	111-69-3	16.976	41	68, 54

Preparation of standard solutions

A total of 19 target compounds were used as standard materials. The individual stock solutions were prepared by diluting each standard compound in DCM to a concentration of 1,000 µg/mL.

A multi-standard solution was prepared by adding 500 µL of each individual stock solution to a 10 mL volumetric flask, resulting in a final concentration of 50 µg/mL for each of the 19 target compounds in DCM.

For calibration curve preparation, the multi-standard solution was further diluted with DCM to obtain standard solutions with final concentrations of 0.1, 0.25, 0.5, 1, 2.5, 5, and 10 µg/mL.

Sample preparation

The method was applied to commercial electrolyte sample containing lithium salts(LiFSI and $LiPF_6$), three organic solvents (EC, EMC, DMC), and four additives (VC, FEC, PS, SN).

For analysis, liquid electrolyte samples were diluted by transferring 0.1 mL of the sample into a 100 mL volumetric flask, resulting in a 1000-fold dilution. Subsequently, to accurately quantify compounds detected at high concentrations, additional dilutions(10-fold or 100-fold) were performed using the initial diluted solution. The final diluted samples were analyzed quantitatively using GC-MS.

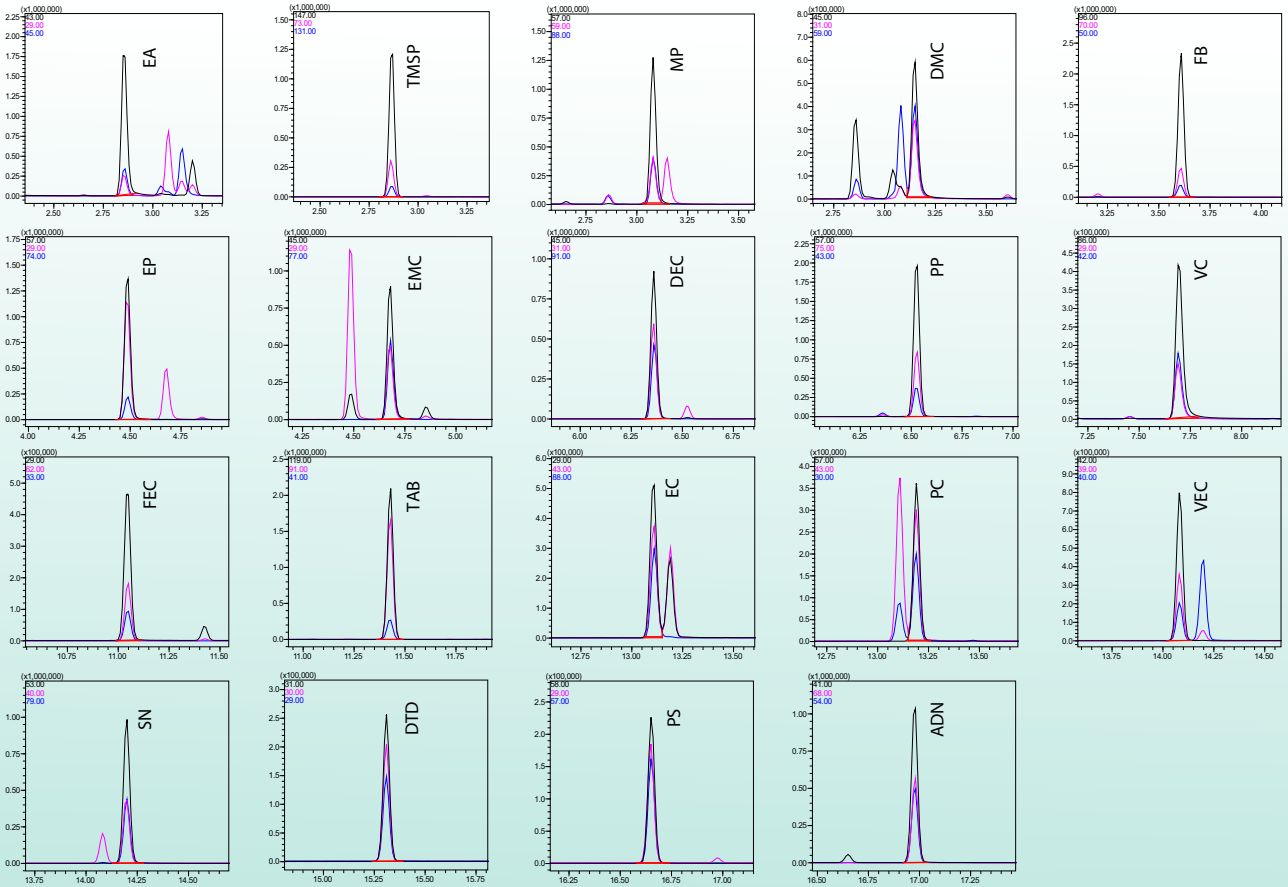


Figure 2. SIM chromatograms of 19 organic solvents and additives (10 µg/mL)

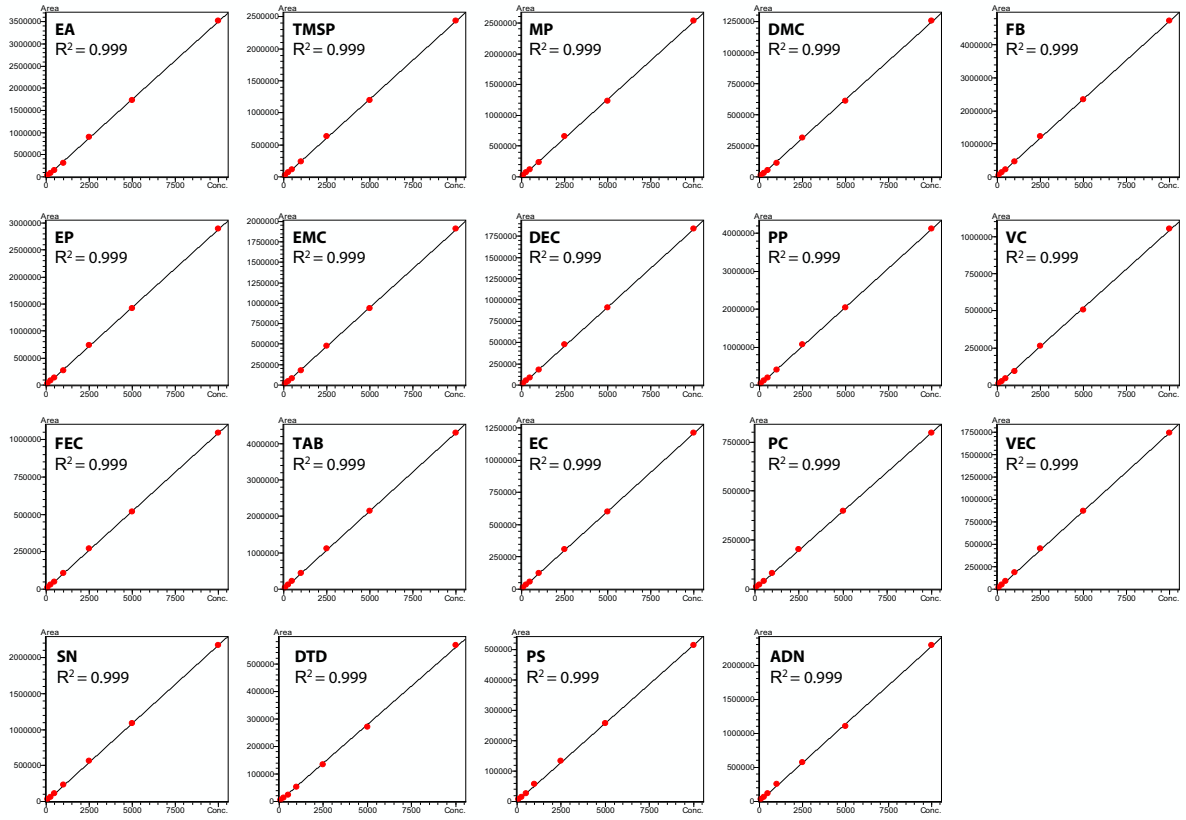


Figure 3. Linearity of calibration curve for 19 target compounds.

Results

The retention times and selected ions listed in Table 2 were determined by analyzing individual standard solutions under optimized GC-MS conditions. For quantification, the ions exhibiting the highest intensity and selectivity were selected. The SIM chromatograms of 19 organic solvents and additives are shown in Figure 2. The calibration curves for all standard compounds are excellent linearity, with correlation coefficients (R^2) greater than 0.999 (Figure 3).

The developed analytical method was successfully applied to actual LIB electrolyte samples, confirming the presence and quantifying the concentrations of three organic solvents (EC, EMC, DMC) and four additives (VC, FEC, PS, SN), as summarized in Table 3.

Table 3. Detected concentrations of organic solvents and additives in commercial LIB electrolyte samples

Compounds	Concentration (mg/mL)
DMC	471.1
EMC	497.4
EC	193.7
VC	30.6
FEC	13.5
PS	3.9
SN	13.4

Conclusions

In this study, a simultaneous GC-MS method was developed and validated for the quantitative analysis of 19 organic solvents and additives in LIB electrolytes. The calibration curves demonstrated excellent linearity for all target compounds. Furthermore, The method was successfully applied to actual LIB electrolyte samples. This analytical method provides a reliable approach for lithium-ion battery research and quality assessment.

Reference

1. Analysis of Carbonic Esters and Additives in Lithium Ion Battery Electrolytes, Application News No.01-00708-EN

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