Analysis of electrolyte components of lithium-ion batteries using gas chromatography-mass spectrometry

Author: Thermo Fisher Scientific Inc.

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Goal

At present, methods and literature references for determining electrolyte composition are limited. The purpose of this work is to establish a simple and efficient gas chromatography–mass spectrometry detection method for a sensitive and fast determination of lithium-ion battery electrolyte composition and content.

Introduction

The electrolyte in a lithium-ion battery is the carrier of positive lithium ions between the cathode and anode. It is generally made of lithium salts dissolved in organic solvents. Electrolyte solutions must enable the Li-ions to transport freely, requiring both high dielectric constant and low viscosity. For this reason, suitable electrolyte solutions are a mixture of cyclic and linear carbonate esters, in which the exact composition plays a key role in the performance of lithium-ion batteries.

Gas chromatography–mass spectrometry can be used to provide the qualitative and quantitative composition of the Li-battery electrolyte, with a direct injection of diluted samples. In this study, a simple GC-MS method has been developed to detect ester compounds in a concentration range of 3.0 μg/L to 30.0 μg/L.

Experimental

Instrumentation

A Thermo Scientific™ TRACE™ 1310 GC connected to a Thermo Scientific™ ISQ™ 7000 single quadrupole mass spectrometer with an electron impact (EI) ionization source was used. A Thermo Scientific™ AS1310 liquid autosampler performed the injection.

The separation of the ester compounds was achieved on a Thermo Scientific™ TraceGOLD™ TG-5MS, 30 m, 0.25 mm i.d., 0.25 μm film thickness, capillary column (P/N 26098-1420).

Reagents and standards

A standard mixture of ester compounds at ≥97% concentration was used to prepare diluted standard solutions in ethyl acetate at five levels of concentration: 4, 10, 20, 50, and 100 mg/L.

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Sample preparation

The sample preparation consisted of dilution of the electrolyte sample to a suitable concentration with ethyl acetate for direct injection into the GC-MS.

GC-MS experimental conditions

The GC-MS experimental conditions are reported in Tables 1 and 2.

Table 1. GC-MS method parameters

GC-MS method parameter	Value
GC column	TraceGOLD TG-5MS 30 m, 0.25 mm i.d., 0.25 µm film thickness (P/N 26098-1420)
GC oven temperature	50 ˚C (3 min), 10 ˚C/min to 240 ˚C (3 min)
Injector	SSL
Injector temperature	280 ˚C
Injection mode	Split 50:1
Injection volume	1 µL
Carrier gas	Helium at 1 mL/min constant flow
MS ion source temperature	EI source at 300 ˚C
Transfer line temperature	280 ˚C
Acquisition mode	Full scan 40–200 m/z

Table 2. Standard mixture composition, retention times, and selected ions

#	Compound	RT (min)	Quant ion	Qual ion
1	EMC (ethyl methyl carbonate)	2.70	45	77
2	VC (vinylene carbonate)	3.38	86	42
3	DEC (diethyl carbonate)	3.96	91	45
4	PP (n-propyl propionate)	4.41	75	57
5	FEC (fluoroethylene carbonate)	5.28	62	106
6	EC (ethylene carbonate)	7.38	88	43
7	PC (propylene carbonate)	7.80	57	87
8	PS (1,3-propane sultone)	11.03	58	122

Results and discussion

Different dilution solvents, including ethyl acetate, acetone, hexane, toluene, ethanol, and trichloromethane, were compared with respect to their dissolving power. The dissolving effect for the target ester compounds was acceptable only with ethyl acetate, which was selected as the dilution solvent for this study. Five levels of concentration were prepared (4, 10, 20, 50, and 100 mg/L) and used to verify the linear response, the limit of detection (LOD), the limit of quantitation (LOQ), and the area counts repeatability (RSD%). An example of the total ion chromatogram of the standard mixture at 20 mg/L is shown in Figure 1.
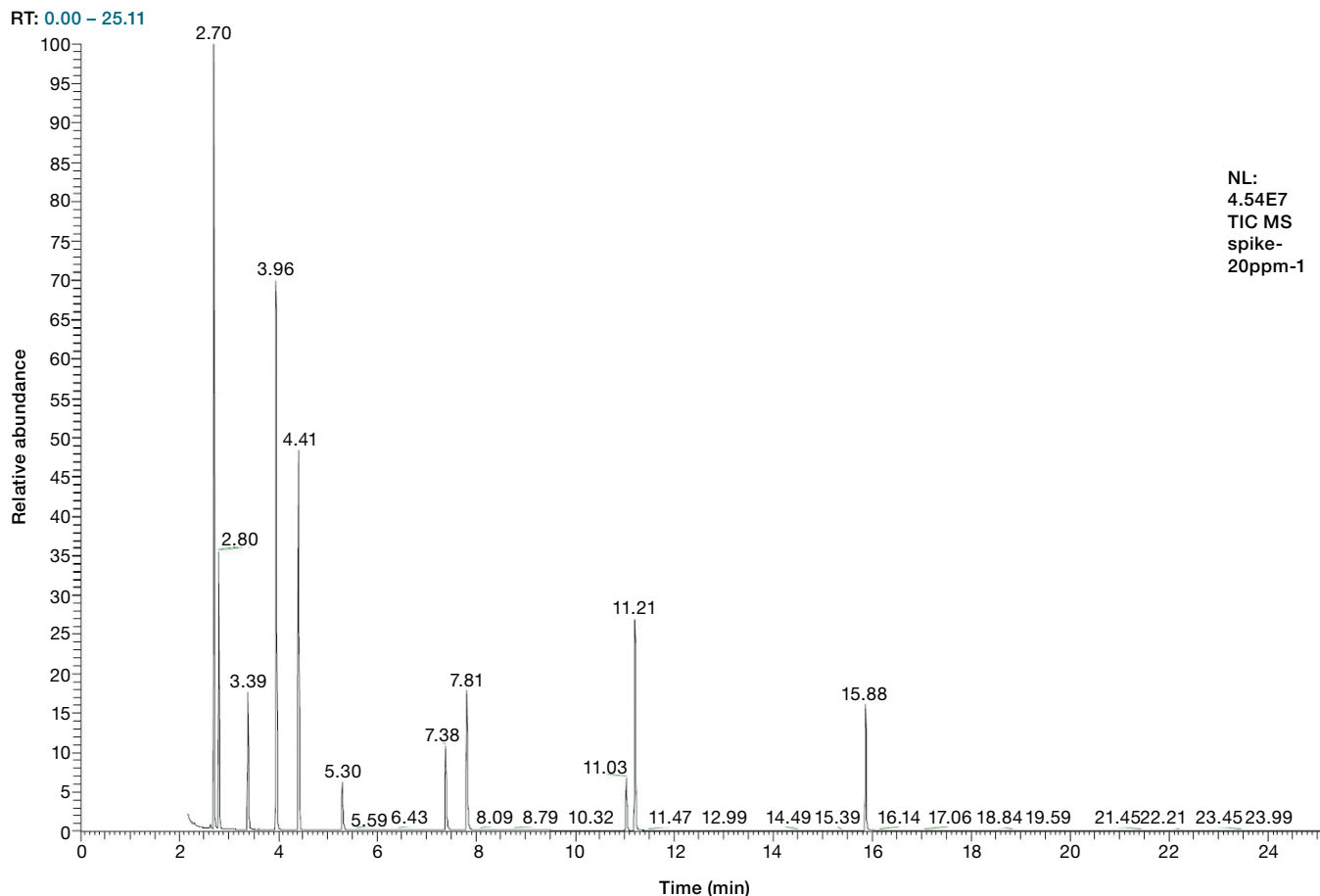

Figure 1. Total ion chromatogram of the standard mixture of esters at 20 mg/L

The linear calibration curves obtained for the ester compounds are reported in Figure 2, showing an excellent linear relationship with correlation coefficients >0.999 between 4.0 and 100.0 mg/L (Table 3).
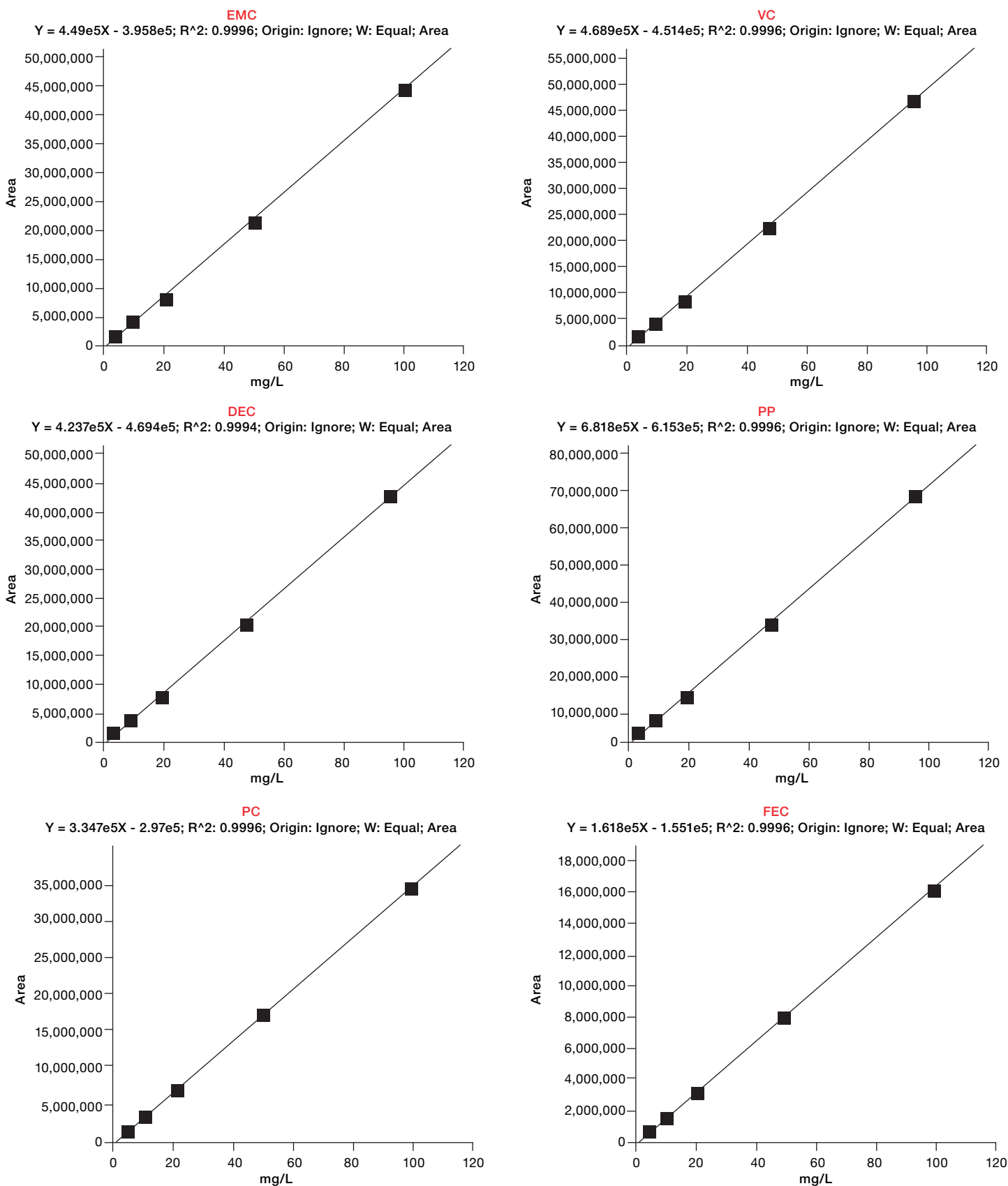

Figure 2. Linear relationship plots for the ester compounds under study

PS
Y = 1.981e5X - 6.191e4; R^2: 0.9998; Origin: Ignore; W: Equal; Area

EC
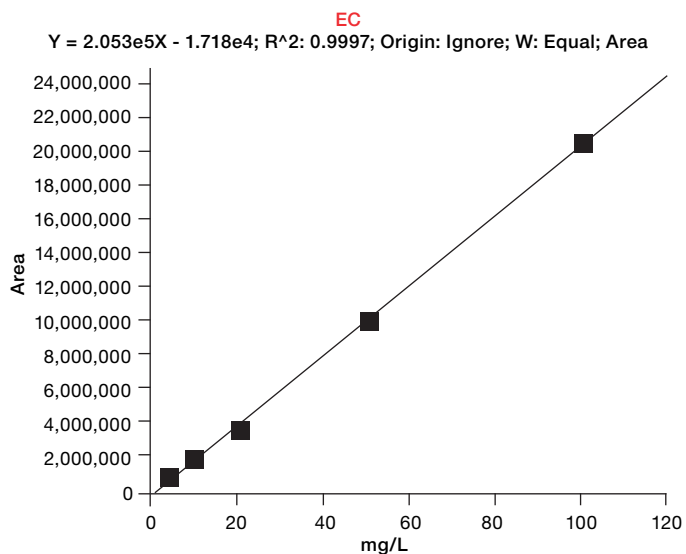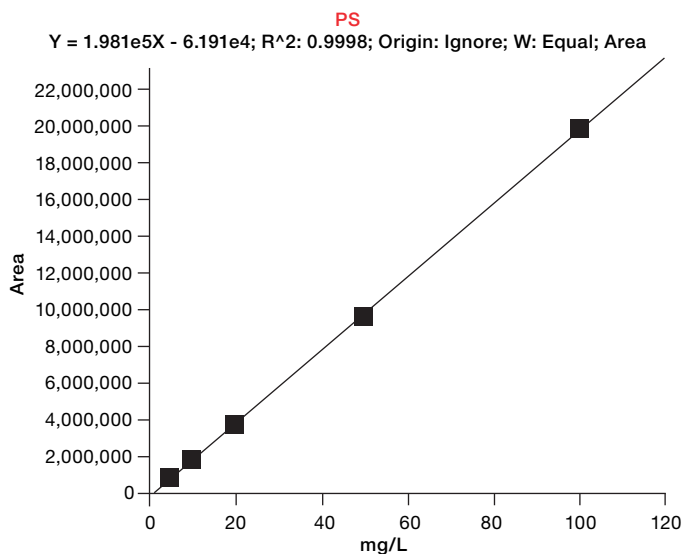Y = 2.053e5X - 1.718e4; R^2: 0.9997; Origin: Ignore; W: Equal; Area

Figure 2 continued. Linear relationship plots for the ester compounds under study

Table 3. Retention time, response linearity, and limit of detection (LOD) for the target analytes

#	Compound	RT (min)	Linear range (mg/L)	Correlation coefficient (R^2)	LOD (µg/L)
1	EMC (ethyl methyl carbonate)	2.70	4.0–100.0	0.9996	3.0
2	VC (carbonated ethyl carbonate)	3.38	4.0–100.0	0.9996	9.0
3	DEC (diethyl carbonate)	3.96	4.0–100.0	0.9994	4.0
4	PP (propylene acid)	4.41	4.0–100.0	0.9996	4.5
5	FEC (fluorocarbonate olesters)	5.28	4.0–100.0	0.9996	28.0
6	EC (ethylene carbonate)	7.38	4.0–100.0	0.9997	32.0
7	PC (acrylic carbonate)	7.80	4.0–100.0	0.9996	19.0
8	PS (1,3-propylene sulfonate lactone)	11.03	4.0–100.0	0.9998	25.0

The limit of detection was extrapolated on the extracted quantification ion, considering a signal-to-noise ratio (S/N) of 3. The LODs for the target ester compounds are reported in Table 3. Full scan acquisition was applied for electrolyte composition screening. However, the sensitivity for the target compounds can be lowered by 1–2 orders of magnitude if necessary by acquiring the signal in Selected Ion Monitoring (SIM) mode.

Sample analysis
Using the established analysis method, the lithium-ion battery electrolyte was diluted with ethyl acetate and spiked with the 20 mg/L standard mixture to evaluate the recovery and the repeatability over six repeated injections, as reported in Table 4.

Table 4. Target analyte recovery and repeatability (n=6)

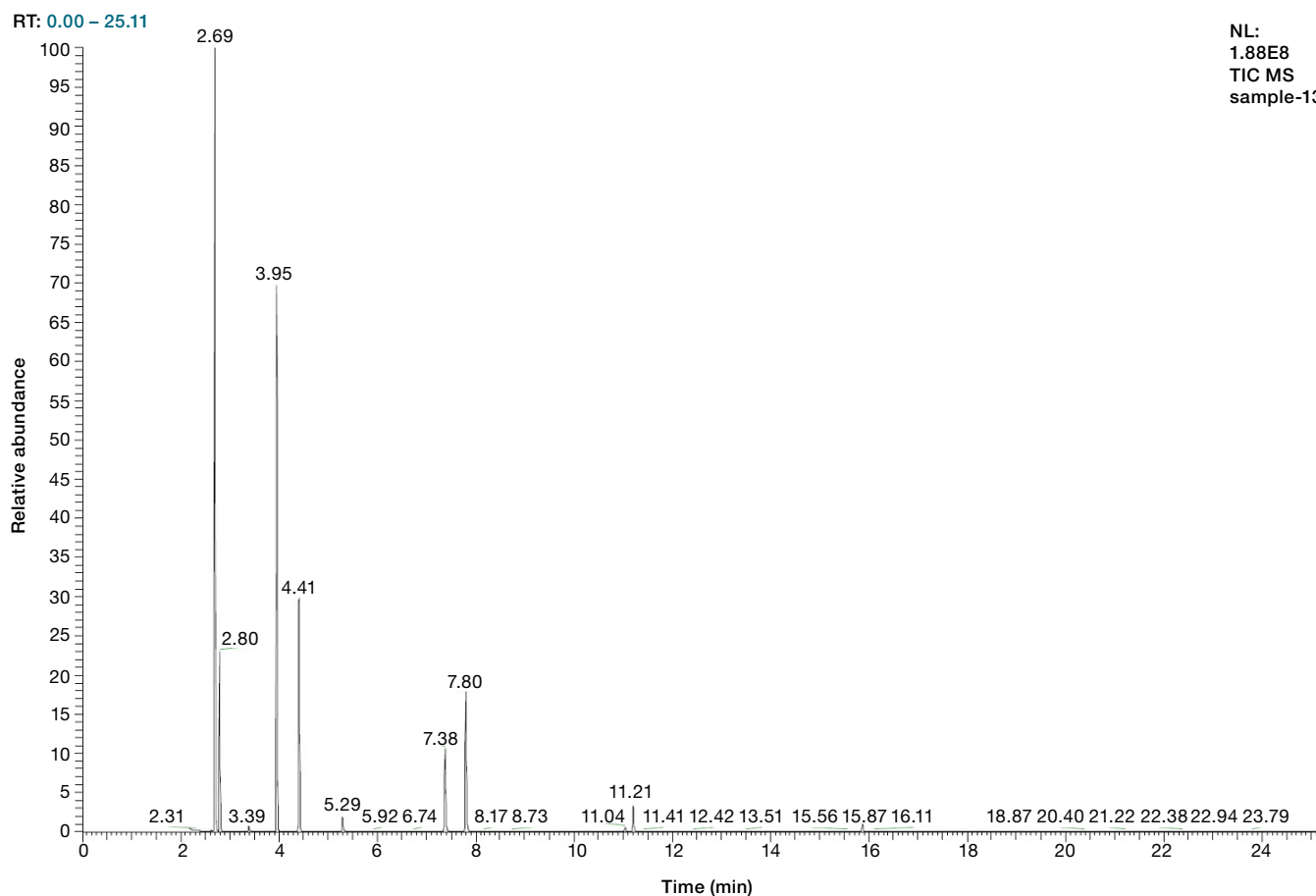| #	Compound	Recovery (%)	RSD (%)
1	EMC (ethyl methyl carbonate)	105.3	3.96
2	VC (carbonated ethyl carbonate)	101.6	1.34
3	DEC (diethyl carbonate)	104.6	3.74
4	PP (propylene acid)	95.2	3.62
5	FEC (fluorocarbonate olesters)	96.3	3.21
6	EC (ethylene carbonate)	94.3	4.16
7	PC (acrylic carbonate)	92.4	4.14
8	PS (1,3-propylene sulfonate lactone)	97.4	3.15

Figure 3. Total ion chromatogram of a diluted electrolyte sample

Conclusion

The GC-MS method is a simple, reliable, and accurate approach for lithium-ion battery electrolyte composition analysis and quality control requirements. The samples can be simply diluted with a suitable solvent and directly injected into the GC-MS system.

The results show very good recovery for the target ester compounds of 92.4.3–105.3%, demonstrating the high accuracy of the method. The excellent precision of the method was also demonstrated, with an RSD value ≤4.16% over six repeated injections.

Full scan acquisition can be applied with good sensitivity. SIM acquisition can be utilized to lower the limits of detection for the method.

References

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