APPLICATION NOTE

Gas Chromatography / Mass Spectrometry

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Determination of Nine Carbonates in Lithium Ion Battery Electrolyte By GC/MS

Introduction

The electrolytic solutions commonly used in commercial lithium batteries consist of lithium salts, organic solvents and some additives. The organic solvents are mainly cyclic carbonates, such as ethylene carbonate and propylene carbonate, or chain carbonates, such as diethyl carbonate and ethyl methyl carbonate. Composition and ratio of these carbonates have important implications for energy density, cycle life and the safety of lithium ion batteries. Therefore, the study of the composition and content of carbonates in the electrolytic solution plays an important role in the development and quality control of lithium ion batteries.

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In this paper, a qualitative and quantitative method for the determination of nine carbonates in electrolytic solutions was established using the PerkinElmer Clarus® SQ 8 GC/MS with electron ionization (EI) source. The method is simple, sensitive and efficient.

Experimental

The PerkinElmer Clarus SQ 8 GC/MS operating in electron ionization (EI) mode was used to perform these experiments with the conditions presented in Table 1. A PerkinElmer Elite 35 MS column (30 m × 0.25 mm × 0.25 µm) was used to separate the eluting compounds.

Table 1. Analytical parameters.

GC Parameters	
Injector Type	Capillary injector with capillary splitless deactivated glass liner with deactivated wool
Inlet Temp	280 °C
Carrier Gas Flow	1 mL/min
Split Flow	20 mL/min
Injection Volume	1 µL
Initial Oven Temp	35 °C
Oven Hold	3.0 min
Ramp	10 °C/min
2nd Oven Temp	240 °C
Oven Hold	2.0 min
MS Parameters	
Mass Range (amu)	25 to 300
GC Inlet Line Temp	280 °C
Ion Source Temp	270 °C
Function Type	SIFI
Ionization	EI

Nine carbonic esters were investigated (shown in Table 2) with calibration standards purchased from ANPEL Laboratory Technologies (Shanghai) Inc. and diluted with ethyl acetate (HPLC grade, Honeywell) to produce the required range of calibration solutions. The electrolytes sample was diluted 1:10000 (v/v) with ethyl acetate before injection into the GC/MS.

Method precision was investigated with six injections of the level 4 spike of standard and diluted sample. Method detection limits were determined by analyzing seven replicates of the level 1 concentration standard. The spike recovery experiment was carried out by analyzing the level 4 spike in a diluted sample.

Results and Discussion

The selected ion chromatogram of a calibration standard is shown in Figure 1. All target compounds were separated using selected ion scanning module. The calibration curves were plotted as the peak area versus the amount of analyte. The determination coefficients (r^2) of all compounds were over 0.999, showing the reliability of the analysis in the range of 1 – 100 mg/L. Table 3 and 4 summarizes the results for retention time, quantitation and qualitative ion, linearity, precision, percent recovery, method detection limits (MDLs) and quantitation limits (MQLs). The MDLs per sample were calculated to be in the range of 0.080 – 0.176 mg/L; the recoveries are in the range of 92.40 – 104.45 % in real samples; the precision data (RSD %) are in the range of 1.02 – 2.16% for the spike of standard sample and 1.61 – 2.05% for the spike of actual sample.

Table 2. Calibration points employed in this study.

Compound Name	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Dimethyl Carbonate	1.00 mg/L	5.00 mg/L	10.00 mg/L	20.00 mg/L	50.00 mg/L	100.00 mg/L
Ethyl Methyl Carbonate	1.00 mg/L	5.00 mg/L	10.00 mg/L	20.00 mg/L	50.00 mg/L	100.00 mg/L
Diethyl Carbonate	1.00 mg/L	5.00 mg/L	10.00 mg/L	20.00 mg/L	50.00 mg/L	100.00 mg/L
n-Propyl Propionate	1.00 mg/L	5.00 mg/L	10.00 mg/L	20.00 mg/L	50.00 mg/L	100.00 mg/L
Vinylene Carbonate	1.00 mg/L	5.00 mg/L	10.00 mg/L	20.00 mg/L	50.00 mg/L	100.00 mg/L
Fluoroethylene Carbonate	0.94 mg/L	4.70 mg/L	9.40 mg/L	18..80 mg/L	47.00 mg/L	94.00 mg/L
Ethylene Carbonate	1.07 mg/L	5.36 mg/L	10.72 mg/L	21.44 mg/L	53.60 mg/L	107.20 mg/L
Propylene Carbonate	1.00 mg/L	5.00 mg/L	10.00 mg/L	20.00 mg/L	50.00 mg/L	100.00 mg/L
1,3-Propanesultone	0.93 mg/L	4.67 mg/L	9.33 mg/L	18.66 mg/L	46.65 mg/L	93.30 mg/L

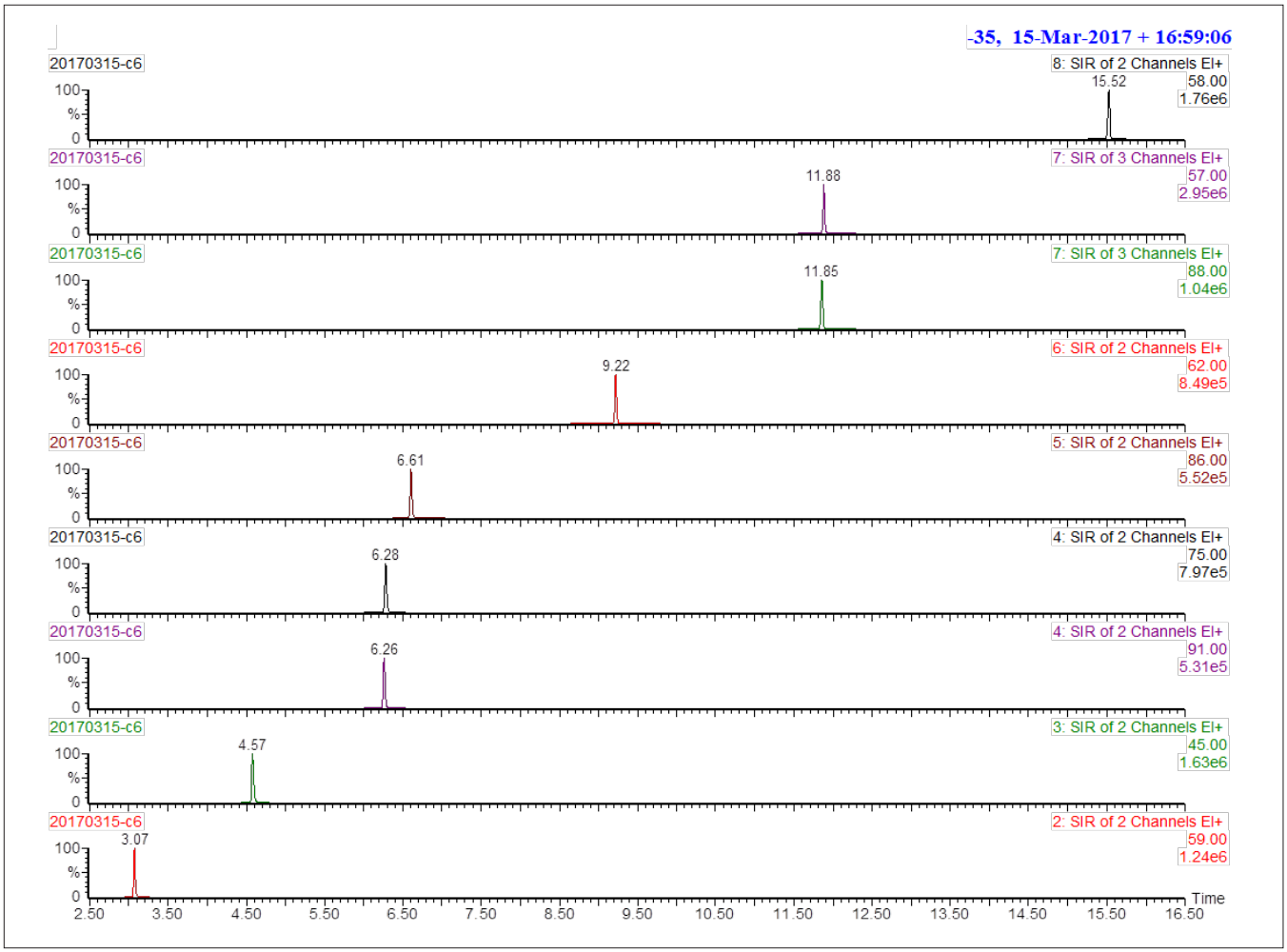

Figure 1. Selected ion chromatogram of a calibration standard (level 6).

Table 3. Results for retention time, quantitation and qualitative ion and linearity.

Compound Name	Retention Time Min	Quantitation Ion	Qualitative Ion	Linearity		
				Slope	Intercept	r^2
Dimethyl Carbonate	3.27	59	90	393.26	-336.28	0.9992
Ethyl Methyl Carbonate	4.65	45	77	1260.78	-694.44	0.9995
Diethyl Carbonate	6.29	91	45	370.98	-237.25	0.9994
n-Propyl Propionate	6.31	75	57	523.27	-524.98	0.9991
Vinylene Carbonate	6.63	86	42	430.77	-396.67	0.9993
Fluoroethylene Carbonate	9.22	62	106	500.50	-351.45	0.9996
Ethylene Carbonate	11.85	88	43	843.19	-456.71	0.9997
Propylene Carbonate	11.87	57	87	2021.70	-1444.29	0.9996
1,3-Propanesultone	15.22	58	122	1434.08	-984.26	0.9997

Table 4. Results for precision, recovery, MDL and MQL.

Compound Name	MDL ug/ml	MQL ug/ml	Precision (RSD %)		Recovery %
			Standard Sample	Actual Sample	
Dimethyl Carbonate	0.111	0.444	1.69	1.97	101.85
Ethyl Methyl Carbonate	0.176	0.705	2.16	1.70	100.60
Diethyl Carbonate	0.172	0.690	1.99	1.61	96.70
n-Propyl Propionate	0.171	0.684	1.90	1.74	92.40
Vinylene Carbonate	0.166	0.664	1.62	1.81	98.10
Fluoroethylene Carbonate	0.104	0.415	1.91	2.05	95.30
Ethylene Carbonate	0.146	0.584	1.34	1.89	104.45
Propylene Carbonate	0.086	0.343	1.02	1.78	93.05
1,3-Propanesultone	0.080	0.320	1.34	1.75	94.05

Summary

In this paper, the method of determination for nine carbonates in lithium ion batteries electrolyte was established using the PerkinElmer Clarus SQ 8 GC/MS with EI source. This method demonstrates results with good precision, recovery, linearity and detection limits. It satisfies the needs of the lithium ion battery industry.

References

Shan-shan. Sun, 2009. Reaserch on a novel electrolyte of ionic liquid used in Li-ion batteries. Dissertation for the masters degree in engineering. Harbin Institute of Technology.

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