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Application News

GC-MS GCMS-QP2020 NX

Using GCMS to Determine the Phthalate Content in E-liquid

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User Benefits

- The phthalate content in e-liquid can be determined in accordance with Method II in the National Food Safety Standards: Determination of Phthalates in Foods (GB 5009.271-2016).
- Using this method, phthalates can be analyzed with good linearity and repeatability for each component.

■ Abstract

The Shimadzu GCMS-QP2020 NX gas chromatograph mass spectrometer was used to determine the phthalate content in several e-liquids. Results revealed that linearity was good for each compound within the concentration range of the calibration curve, and correlation coefficients were all above 0.998. A standard mixture at a concentration of 0.10 µg/mL was injected six times consecutively to determine repeatability. Repeatability was good, with the relative standard deviation (RSD%) of the peak area less than 10 % for all of the compounds. That method can be used as a reference to determine the phthalate content in e-liquids.

■ Introduction

E-liquid is heated by an atomizer in e-cigarettes to produce vapor-like smoke from a cigarette. E-liquid mostly consists of a base (glycerin, propylene glycol, water, etc.) and additives (flavorings, plant extracts, etc.). Impurities that are toxic and harmful to humans, such as phthalates, can be introduced during the production and packaging of an e-liquid. Phthalates act like estrogen in humans and animals, where they can interfere with endocrine secretion and affect liver and kidney functions.

In light of the rapid increase in e-cigarettes and safety issues with such products, a growing number of countries and civil organizations are already developing standards to start regulating e-cigarettes. The China Electronics Chamber of Commerce is developing an organizational standard, "Technical specification for safety of e-liquid" (draft for comment), that strictly limits many impurities in e-liquid. The standard stipulates that the total concentration of phthalates should be less than 60 mg/kg. Therefore, a method of determining the phthalate content in e-liquid using a Shimadzu GCMS-QP2020 NX gas chromatograph mass spectrometer was devised based on requirements in "Technical specification for safety of e-liquid" (draft for comment) and in accordance with Method II in the National Food Safety Standards: Determination of Phthalates in Foods (GB 5009.271-2016). This method can effectively monitor the phthalate concentrations in e-liquid.

■ System

Analytical conditions are shown in Table 1.

Table 1 Analytical Conditions

GCMS System	: GCMS-QP2020 NX
Analytical Column	: SH-I-5Sil MS, 30 m × 0.25 mm × 0.25 µm
Column Temp. Program	: 60 °C (1 min) - 20 °C/min - 220 °C (1min) - 5 °C/min - 250 °C (1min) - 20 °C/min - 290 °C (7.5 min)
Injection Temp.	: 260 °C
Carrier Gas Control Mode	: Constant flow (1 mL/min)
Injection Mode	: Splitless
Injection Volume	: 1 µL
Ionization Mode	: EI
Ion Source Temp.	: 230 °C
Interface Temp.	: 280 °C
Data Acquisition Mode	: SIM

■ Sample Preparation

The steps for sample preparation are shown in Fig. 1.

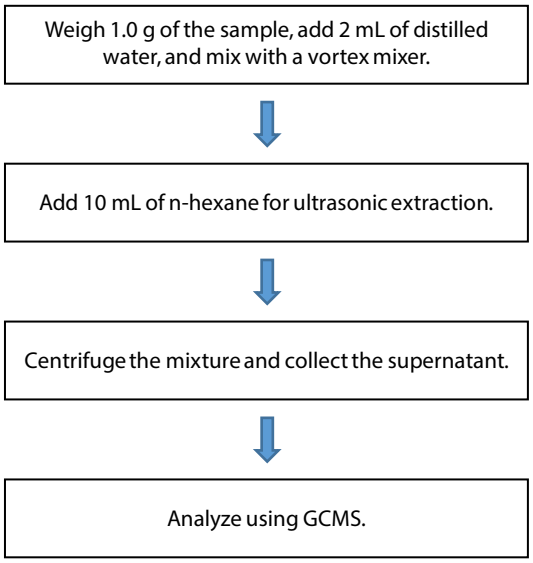

Fig. 1 Workflow of Sample Preparation

■ Chromatogram for Standards

Compounds in the standards and corresponding SIM information are shown in Table 2. The TIC chromatogram for the phthalate standards and mass chromatograms for some of the compounds are shown in Fig. 2 and Fig. 3, respectively.

Table 2 Compounds, Retention Times, and Selected Ions

No.	Compound	Abbreviation	Retention Time (min)	CAS No.	Quantitative Ion (*m/z*)	Qualitative Ion (*m/z*)
1	Dimethyl phthalate	DMP	7.740	131-11-3	163	77, 194
2	Diethyl phthalate	DEP	8.605	84-66-2	149	177, 105
3	Diallyl phthalate	DAP	9.522	131-17-9	149	189, 132
4	Diisobutyl phthalate	DIBP	10.351	84-69-5	149	223, 163
5	Dibutyl phthalate	DBP	11.116	84-74-2	149	223, 205
6	Bis(methylglycol) phthalate	DMEP	11.415	117-82-8	149	104, 176
7-1	Bis(4-methylpentyl) phthalate	BMPP-1	12.102	146-50-9	149	85, 167
7-2	Bis(4-methylpentyl) phthalate	BMPP-2	12.138	146-50-9	149	85, 167
8	Bis(2-ethoxyethyl) phthalate	DEEP	12.491	605-54-9	149	104, 193
9	Di-n-pentyl phthalate	DPP	12.930	131-18-0	149	237, 219
10	Di-n-hexyl phthalate	DHXP	15.126	84-75-3	149	251, 233
11	Butyl benzyl phthalate	BBP	15.258	85-68-7	149	91, 206
12	Bis(2-butoxyethyl) phthalate	DBEP	16.739	117-83-9	149	101, 193
13	Dicyclohexyl phthalate	DCHP	17.473	84-61-7	149	167, 249
14	Bis(2-ethylhexyl) phthalate	DEHP	17.641	117-81-7	149	167, 279
15	Diphenyl phthalate	DPhP	17.764	84-62-8	225	77, 104
16	Dioctyl phthalate	DNOP	19.402	117-84-0	279	261
17	Diisononyl phthalate	DINP	19.802	28553-12-0	293	127
18	Dinonyl phthalate	DNP	21.141	84-76-4	149	293, 275

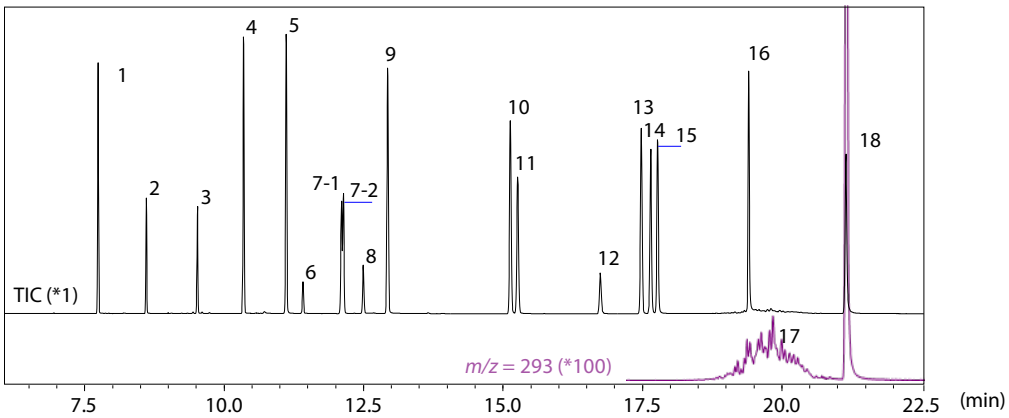

Fig. 2 TIC Chromatogram for the Phthalate Standards and the *m/z* 293 Ion Peak for DINP (No. 17)

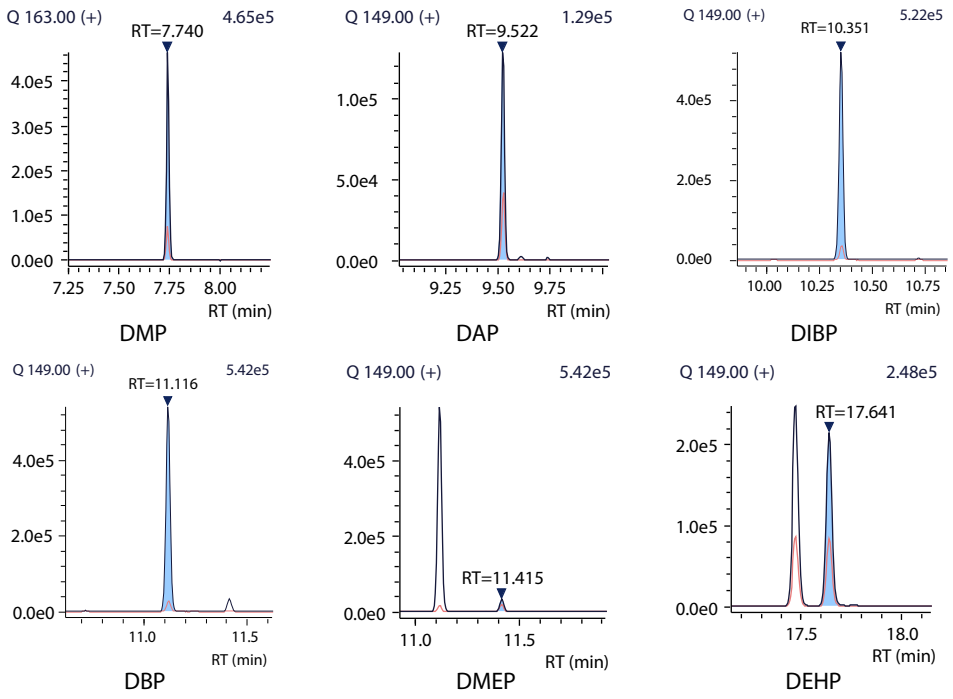

Fig. 3 Mass Chromatograms for Some of the Compounds

■ Calibration Curves and Detection Limits

Appropriate amounts of phthalate standard mixtures were used to prepare a series of standard mixtures at concentrations of 0.02, 0.05, 0.10, 0.20, 0.50, and 1.00 µg/mL (with DINP concentrations of 0.05, 0.10, 0.20, 0.50, 1.00, or 2.00 µg/mL). The standard samples were mixed well and then injected into the GCMS. The calibration curve was created with the concentration on the horizontal axis and the peak area on the vertical axis.

Calibration curves for some of the target compounds are shown in Fig. 4. Linear correlation coefficients and detection limits are shown in Table 3. The detection limit (S/N = 3) was calculated based on a standard mixture at a concentration of 0.02 µg/mL.

■ Repeatability Results

The standard mixture with a concentration of 0.10 µg/mL was analyzed six times consecutively to determine repeatability. Results are shown in Table 4.

Table 3 Linear Correlation Coefficient and Detection Limit for Phthalates

No.	Compound	Correlation Coefficient	Detection Limit (µg/L)	No.	Compound	Correlation Coefficient	Detection Limit (µg/L)
1	DMP	0.9999	0.419	10	DHXP	0.9991	0.124
2	DEP	0.9998	0.042	11	BBP	0.9995	0.547
3	DAP	0.9993	0.806	12	DBEP	0.9989	2.697
4	DIBP	0.9999	0.100	13	DCHP	0.9993	0.364
5	DBP	0.9998	0.076	14	DEHP	0.9992	0.462
6	DMEP	0.9997	1.826	15	DPhP	0.9996	0.285
7	BMPP	0.9998	0.589	16	DNOP	0.9995	1.913
8	DEEP	0.9995	1.033	17	DINP	0.9999	18.072
9	DPP	0.9997	0.132	18	DNP	0.9986	0.486

Table 4 Repeatability Results (n = 6)

No.	Compound	Peak Area						RSD (%)
		1	2	3	4	5	6	
1	DMP	98179	95717	93086	92755	90819	88237	3.8
2	DEP	74600	76436	75555	76306	73038	71851	2.5
3	DAP	24668	23595	23088	22837	22545	21730	4.3
4	DIBP	127494	123539	121929	119706	118646	113924	3.8
5	DBP	143411	139966	138540	135708	133941	130013	3.5
6	DMEP	8041	7979	7870	7910	7792	7456	2.6
7	BMPP	62772	60659	60026	59133	58188	56702	3.5
8	DEEP	14150	13643	13477	12697	13076	12646	4.4
9	DPP	130036	126151	124129	121188	119137	116086	4.1
10	DHXP	108919	104514	103818	100813	101093	96708	4.0
11	BBP	47747	45250	45536	43210	44561	41229	5.0
12	DBEP	11281	11892	10671	11414	10476	10879	4.7
13	DCHP	80351	77818	76086	74686	74084	72071	3.9
14	DEHP	61299	59182	58805	56661	55729	54393	4.4
15	DPhP	85334	82931	80934	78396	78314	75424	4.5
16	DNOP	6574	6066	5715	5533	5412	5160	8.8
17	DINP	5916	5719	5713	5637	5879	5339	3.6
18	DNP	77482	72147	70434	67688	67475	65865	6.0

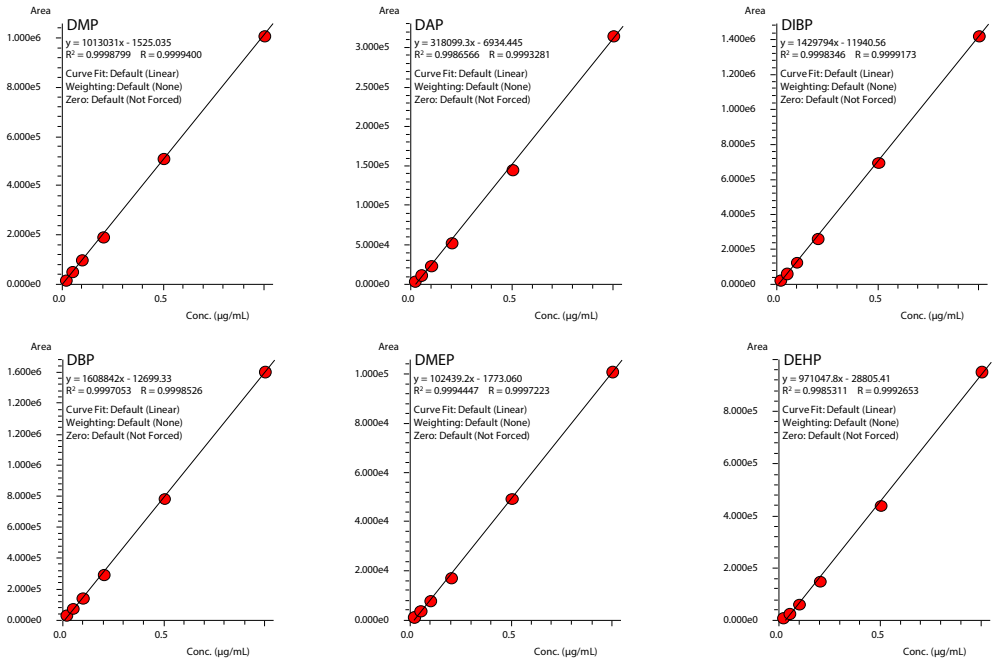

Fig. 4 Calibration Curves for Some Phthalates

■ Quantitative Results and Recovery Rates of Real Samples

Three samples of an apple cocktail-flavored e-liquid were prepared according to the sample preparation process indicated in Fig. 1 and used for the spiking and recovery testing. The concentration of the standard spiking mixture was 2.00 mg/kg, with corresponding recovery rates shown in Table 5. Samples of three flavors of commercially available e-liquids were analyzed, with mass chromatograms of detected peaks for those samples shown in Fig. 5. The results are shown in Table 5. Quantitative values (µg/mL) were converted to sample concentrations (mg/kg) in consideration of sample preparation.

■ Conclusion

A method for determining the phthalate content in e-liquid samples using a Shimadzu GCMS-QP2020 NX gas chromatograph mass spectrometer was developed in accordance with Method II of the National Food Safety Standards: Determination of Phthalates in Foods (GB 5009.271-2016). The linearity of the calibration curve for each compound was good, and the correlation coefficient was more than 0.998. A standard mixture at a concentration of 0.10 µg/mL was analyzed six times consecutively to determine repeatability. The RSD% was less than 10 % for each compound. In the spiking and recovery test, the recovery rate was within 67 to 118 % when 2.00 mg/kg of the standard mixture was added. The method can be used as a reference to determine the phthalate content in e-liquid samples.

Food flavorings in e-liquid will also be regulated in China. The analysis method is introduced in Application News "Using GCMS to Determine the 2,3-Butanedione, 2,3-Pentanedione, and Acetoin Content in E-liquid"(03-GCMS-415-EN)

Table 5 Quantitative Results and Recovery Rates from Real Samples

No.	Compound	Sample Concentration (mg/kg)			Mean Concentration after Addition of Standard Mixture (mg/kg) (n = 3)	Recovery Rate (%)	RSD (%) (n = 3)
		Apple Cocktail-Favored	Watermelon-Flavored	Banana-Flavored			
1	DMP	N.D.	N.D.	N.D.	1.49	74	1.4
2	DEP	N.D.	N.D.	N.D.	1.34	67	1.0
3	DAP	N.D.	N.D.	N.D.	1.88	94	1.4
4	DIBP	0.12	0.13	0.12	1.80	84	1.2
5	DBP	0.49	0.37	0.35	2.42	96	6.0
6	DMEP	N.D.	N.D.	N.D.	1.41	71	0.6
7	BMPP	N.D.	N.D.	N.D.	1.34	67	1.6
8	DEEP	N.D.	N.D.	N.D.	1.84	92	3.0
9	DPP	N.D.	N.D.	N.D.	1.93	96	1.0
10	DHXP	N.D.	N.D.	N.D.	2.18	109	1.2
11	BBP	N.D.	N.D.	N.D.	1.96	98	1.4
12	DBEP	N.D.	N.D.	N.D.	2.22	111	2.3
13	DCHP	N.D.	N.D.	N.D.	2.04	102	1.8
14	DEHP	0.37	0.35	0.31	2.11	87	2.2
15	DPhP	N.D.	N.D.	N.D.	2.12	106	1.6
16	DNOP	N.D.	N.D.	N.D.	2.28	114	5.1
17	DINP	N.D.	N.D.	N.D.	2.37	118	4.0
18	DNP	N.D.	N.D.	N.D.	2.39	74	6.2

Note: N.D. indicates "not detected."

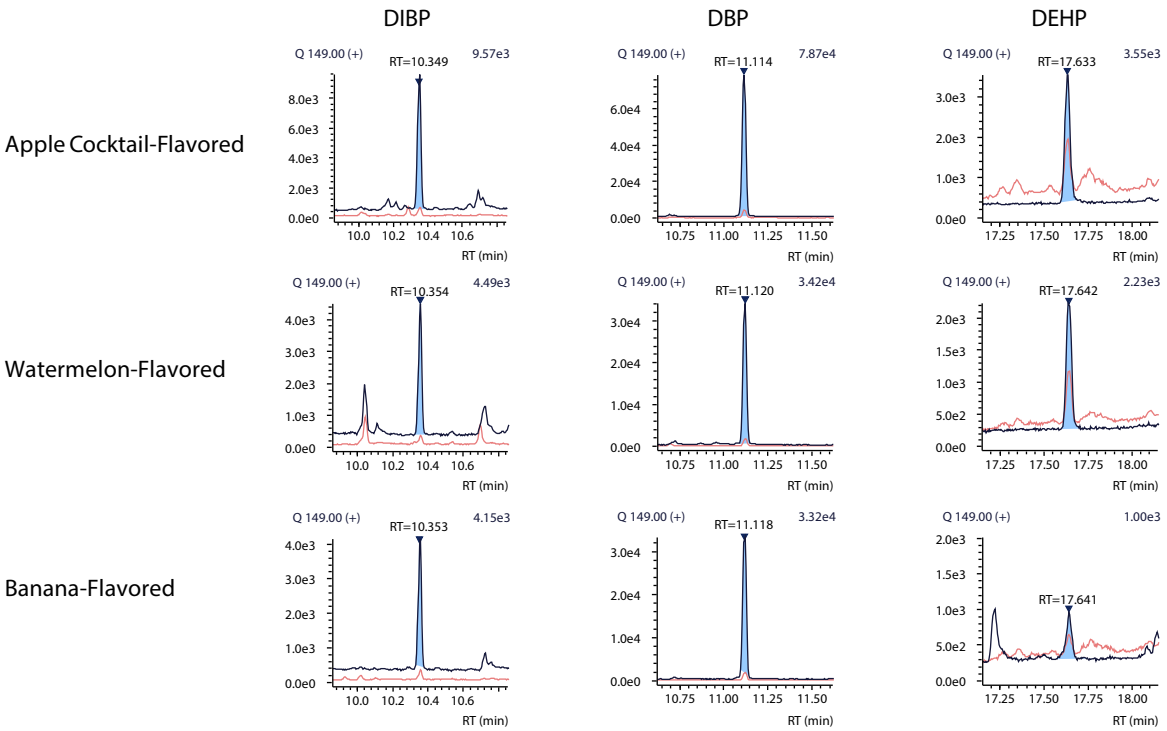

Fig. 5 Mass Chromatograms of Peaks Detected in Samples of Three E-liquid Flavors

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