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Identification and Quantification of 19 Phthalic Acid Esters in Chinese Liquors Using GC-MS/MS

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1. Introduction

Some phthalate acid esters (PAEs) are suspected of producing teratogenic or endocrine-disrupting effects. Considering liquor hobby and risk of PAEs pollution resulted from high alcohol content, it is necessary to establish a detection method in order to provide a basis for risk assessment.

To develop a simple, accurate and cost-effective method, GC/MS/MS, with liquid-liquid extraction after water bath heating, is used for identification and quantification of 19 PAEs in Chinese liquors. Water bath heating is used to remove most ethanol and aroma components to improve extraction efficiency as well as decrease interference. In addition, identification of PAEs with similar structure should be made more convenient and accurate, using a gas chromatograph coupled with a triple quadrupole mass spectrometer.

2. Method and Materials

Sample Preparation

Accurate pipette 10 mL sample to 25 mL vial, water bath heating for 30 min at 85 °C, in which condition most ethanol and aroma components are removed. After cooling to room temperature, add 2 mL n-hexane and vortex for 1 min. Transfer after phase separation an aliquot of the n-hexane phase into a suitable autosampler vial and analyze. Sample may be prepared in approx. 30 min, thus significant time and cost savings were achieved compared to routine method.

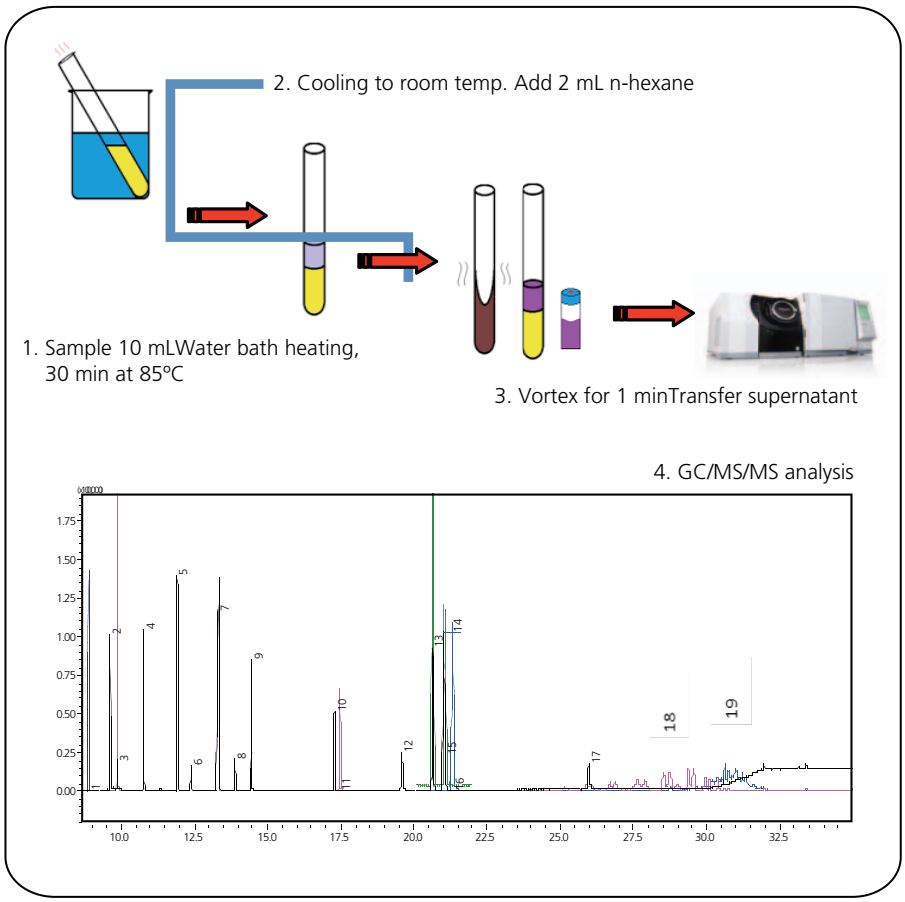

Fig. 1 Sample pre-treatment step & chromatograms of 19 PAEs standards

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Table 1 List of analytes for PAEs using GC-MS/MS

NO.	NAME	CAS NO.	Quantitative transition	Collision voltage(V)	Qualitative transition	Collision voltage(V)
1	Phthalic Acid Diisopropyl Ester	605-45-8	209>149	10	167>149	10
2	Phthalic Acid Diallyl Ester	131-17-9	132>104	7	189>105	17
3	Phthalic Acid Dipropyl Ester	131-16-8	209>149	8	191>149	5
4	Phthalic Acid Diisobutyl Ester	84-69-5	223>149	10	205>149	5
5	Phthalic Acid Dibutyl Ester	84-74-2	223>149	10	205>149	5
6	Phthalic Acid Bis(2-methoxyethyl) Ester	117-82-8	207>59	5	176>149	10
7	Bis (4-methyl-2-pentyl) phthalate	146-50-9	167>149	10	251>149	20
8	Bis(2-ethoxyethyl)phthalate	605-54-9	176>149	10	176>104	25
9	Phthalic Acid Dipentyl Ester	131-18-0	237>149	10	219>149	5
10	Phthalic Acid Dihexyl Ester	84-75-3	251>149	15	233>149	5
11	Phthalic Acid Benzyl Butyl Ester	85-68-7	206>149	10	238>104	20
12	Bis(2-butoxyethyl) Phthalate	117-83-9	193>149	15	176>149	10
13	Phthalic Acid Dicyclohexyl Ester	84-61-7	167>149	10	249>149	15
14	Phthalic Acid Bis(2-ethylhexyl) Ester	117-81-7	167>149	10	279>149	15
15	Phthalic acid,bis-n-heptyl ester	3648-21-3	249>149	10	167>149	15
16	Phthalic Acid Diphenyl Ester	84-62-8	225>77	25	225>141	20
17	Phthalic Acid Di-n-octyl Ester	117-84-0	279>149	12	279>71	17
18	Phthalic Acid Diisononyl Ester (mixture of branched chain isomers)	68515-48-0	293>149	10	293>167	5
19	Phthalic Acid Diisodecyl Ester (mixture of branched chain isomers)	26761-40-0	307>149	20	307>167	5

GC/MS/MS Analysis

Treated samples were analyzed in MRM mode using a gas chromatograph coupled with a triple quadrupole mass spectrometer (GCMS-TQ8030, Shimadzu Corporation, Japan).

Analytical Conditions

GC

Carrier gas	: He
linear velocity	: 37 cm/sec
Injection mode	: Splitless (1 min)
Injection port temperature	: 250°C
Column	: Rxi-5 Sil ms, 30 m × 0.25 mm, 0.25 µm
Temperature program	: 90°C (1 min) - 15°C/min - 210°C (2 min) - 5°C/min - 250°C (5 min) - 25°C/min - 300°C (4 min)

Mass

Ionization	: EI
Collision gas	: Argon
Solvent cutting time	: 4 min
Ion source temperature	: 230°C
Interface temperature	: 280°C
Detector voltage	: tuning voltage + 0.3kV
Monitoring mode	: MRM (Table 1)

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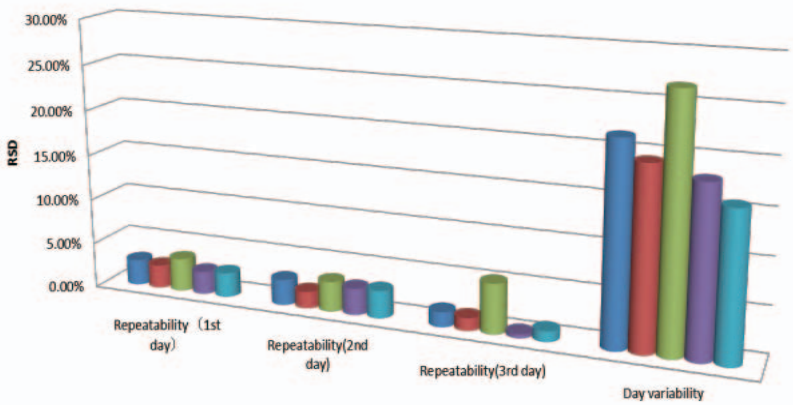
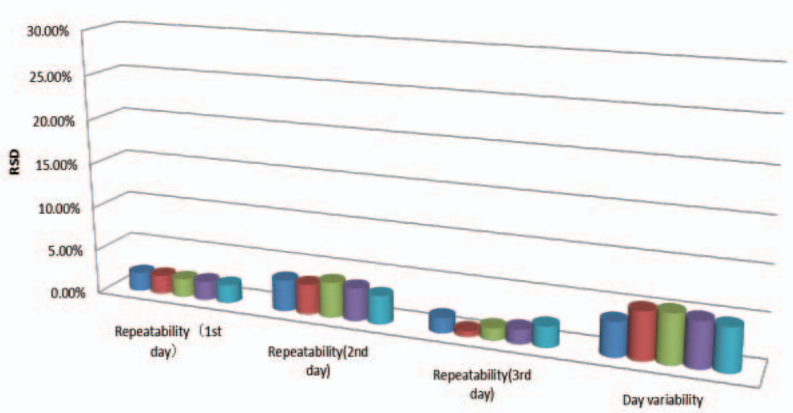
Comparison of SIM and MRM

19 PAEs standard (1 mg/L) were analyzed in SIM mode and MRM mode in this paper. The results show that, regardless of the SIM mode or MRM mode, the RSDs of repeatability within a day for three consecutive days were less than 6%. However, day-to-day validations in MRM mode were less than 6% ,while in SIM mode the peak area showed a decreasing trend with the increase in a number of days and day-to-day validations were more than 15%. From this perspective, GC/MS/MS in MRM mode should be a more stable method.



	Repeatability（1st day）	Repeatability(2nd day)	Repeatability(3rd day)	Day variability
Phthalic Acid Dibutyl Ester	2.83%	2.80%	1.62%	21.62%
Phthalic Acid Bis(2-methoxyethyl) Ester	2.52%	1.82%	1.37%	19.39%
Bis（4-methyl-2-pentyl）phthalate	3.61%	3.28%	5.42%	26.77%
Bis(2-ethoxyethyl)phthalate	2.49%	2.89%	0.44%	18.09%
Phthalic Acid Dipentyl Ester	2.66%	3.01%	1.12%	15.86%

Fig. 2 RSDs of repeatability and reproducibility in SIM mode (n=5)



	Repeatability（1st day）	Repeatability(2nd day)	Repeatability(3rd day)	Day variability
Phthalic Acid Dibutyl Ester	2.10%	3.53%	1.69%	3.79%
Phthalic Acid Bis(2-methoxyethyl) Ester	2.11%	3.38%	0.61%	5.30%
Bis（4-methyl-2-pentyl）phthalate	2.05%	3.96%	1.33%	5.46%
Bis(2-ethoxyethyl)phthalate	2.12%	3.68%	1.59%	5.06%
Phthalic Acid Dipentyl Ester	2.06%	3.18%	2.30%	4.81%

Fig. 3 RSDs of repeatability and reproducibility in MRM mode (n=5)

3. Results and Discussion

MRM provides multiple dimensions for identification. Improved selectivity and sensitivity of the instrumental analysis was achieved by GC/MS/MS technique (Fig. 4 & Table 2). Some PAEs were detected while GC/MS not. Problematic interferences decreased significantly compared to GC/MS, and the LODs of 19 PAEs was 0.02-21.45 μg/L. In addition, removing ethanol before the liquid-liquid extraction procedure resulted in significant improvement of the recovery, within the range of 70-125%.

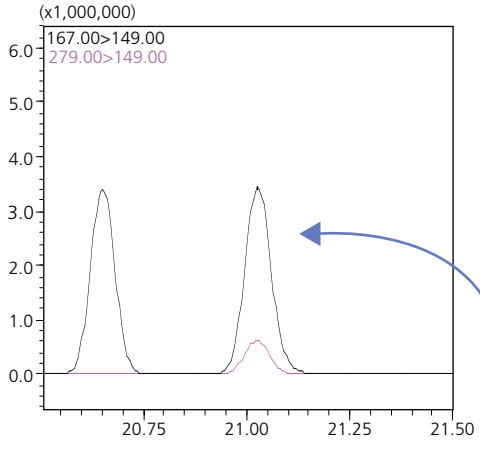


Fig. 4 MRM chromatograms of DEHP

Table 2 LODs and recovery of 19 PAEs

NO.	Compound	LOD (μμg/L)	Recovery (%)
1	Phthalic Acid Diisopropyl Ester	0.05	93.48
2	Phthalic Acid Diallyl Ester	0.82	85.52
3	Phthalic Acid Dipropyl Ester	0.09	96.18
4	Phthalic Acid Diisobutyl Ester	0.56	106.50
5	Phthalic Acid Dibutyl Ester	0.18	108.01
6	Phthalic Acid Bis(2-methoxyethyl) Ester	1.35	75.94
7	Bis（4-methyl-2-pentyl） phthalate	0.04	119.05
8	Bis(2-ethoxyethyl)phthalate	0.25	116.00
9	Phthalic Acid Dipentyl Ester	0.19	108.32
10	Phthalic Acid Dihexyl Ester	0.18	112.73
11	Phthalic Acid Benzyl Butyl Ester	0.11	118.92
12	Bis(2-butoxyethyl) Phthalate	0.99	93.21
13	Phthalic Acid Dicyclohexyl Ester	0.38	93.90
14	Phthalic Acid Bis(2-ethylhexyl) Ester	0.13	116.20
15	Phthalic acid,bis-n-heptyl ester	0.02	124.15
16	Phthalic Acid Diphenyl Ester	0.05	113.33
17	Phthalic Acid Di-n-octyl Ester	0.96	100.94
18	Phthalic Acid Diisononyl Ester (mixture of branched chain isomers)	19.78	103.15
19	Phthalic Acid Diisodecyl Ester (mixture of branched chain isomers)	21.45	102.02

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4. Conclusions

- A simple, accurate and cost-effective method of identification and quantification of 19 phthalate acid esters in Chinese liquors was developed.
- Water bath heating is used to remove most ethanol and aroma components to improve extraction efficiency as well as decrease interference.
- Improved selectivity and sensitivity of the instrumental analysis was achieved by GC/MS/MS technique.

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