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Determination of 20 PAEs in Alcoholic Drinks by Using Ultra High Performance Liquid Chromatography-Tandem Mass Spectrometry

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Introduction

Phthalate esters (PAEs) are a group of commercial chemicals widely used to make plastics more malleable and help lotions penetrate skin. A number of phthalate esters are known to cause birth defects or reproductive harm. As known, alcoholic drinks have always been popular around the world. In alcoholic drinks production, plastic containers are typically used in the storage and transportation process, which could make some phthalate esters leak easily from PVC tubes or vessels as well as plastic caps. The aim of this study is to determine the level of phthalate esters migration in alcoholic drinks by fast liquid chromatography-electrospray tandem mass spectrometry. This method is simple and rapid with acceptable sensitivity to meet the requirements for the analysis of PAEs in alcoholic drinks.

Experimental

Sample pretreament

Accurately weight 5.0 g alcoholic drinks into a glass tube. After centrifugation for 20 min at 6000 rpm, the supernatant was analyzed by LC-MS/MS.

Instrument

The analyses were performed on a Shimadzu Nexera UHPLC instrument (Kyoto, Japan) equipped with LC-30AD pump, CTO-30A column oven, DGU-30A3 degasser, and SIL-30AC autosampler.
A triple quadruple mass spectrometer (Shimadzu LCMS-8040, Kyoto, Japan) was connected to the Shimadzu fast-analytical UHPLC instrument via an ESI interface.

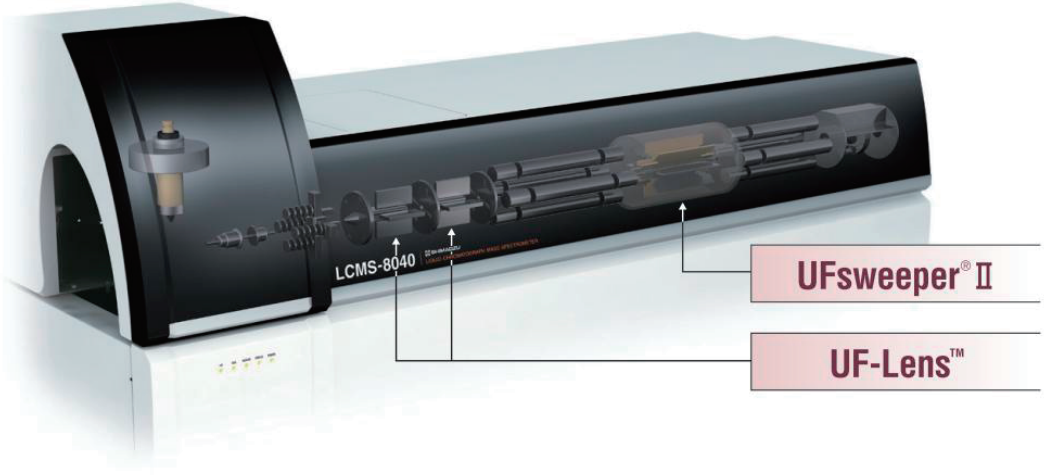

Figure 1 Shimadzu LCMS-8040

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Analytical Conditions

HPLC (Nexera UHPLC system)	
Analytical Column	: Shim-pack XR-ODS III (150 mm x 2.0 mmID, 2.2 µm)
Impurity Delay Column	: Inertsil® ODS-4 (50 mm x 3.0 mmID, 2 µm)
Mobile Phase A	: 5 mM ammonium acetate
Mobile Phase B	: Methanol
Flow Rate	: 0.35 mL/min
Column Temperature	: 45 °C
Injection Volume	: 10 µL
Mass (LCMS-8040 triple quadrupole mass spectrometer)	
Ionization	: ESI
Polarity	: Positive
Probe Voltage	: +4.5 kV (ESI-Positive mode)
Nebulizing Gas Flow	: 3.0 L / min
Drying Gas Flow	: 15 L / min
DL Temperature	: 250 °C
BH Temperature	: 450 °C
Dwell Time	: 15 ms
Pause Time	: 3 ms
Scan Mode	: MRM

Results

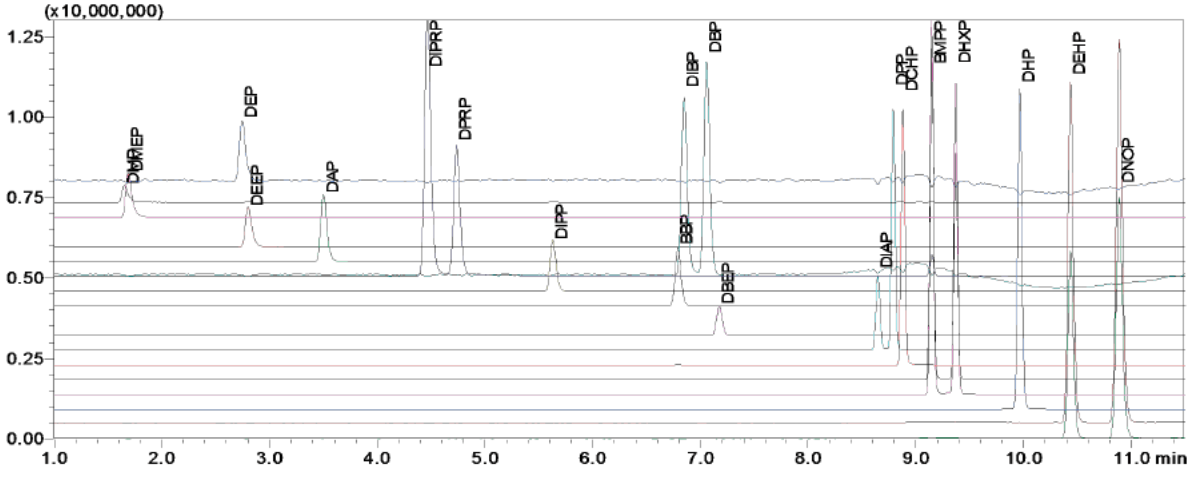

Figure 2 MRM Chromatograms of 20 PAEs (200 µg/L each)

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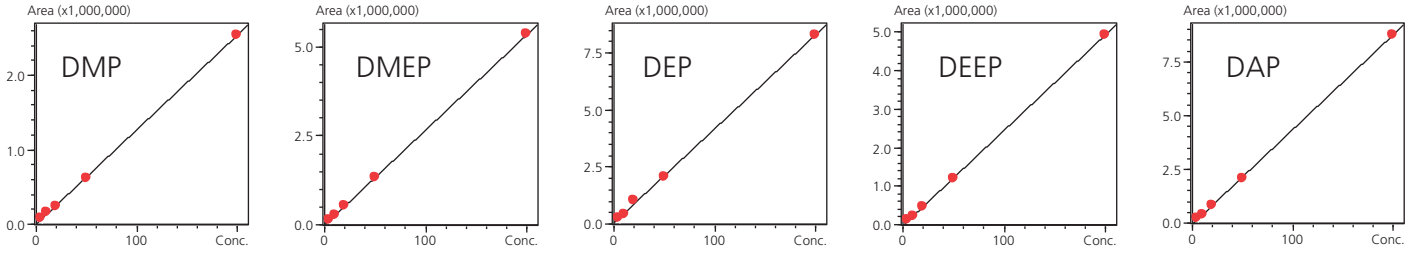

Figure 3 Calibration curves of PAEs

Table 1 Repeatability of PAEs (n=6)

Compound	RSD% (20 µg/L)		RSD% (50 µg/L)		RSD% (100 µg/L)	
	Area	R.T.	Area	R.T.	Area	R.T.
DMP	3.23	0.08	3.14	0.21	1.76	0.24
DMEP	0.73	0.08	0.71	0.19	0.74	0.20
DEP	4.79	0.17	3.90	0.18	2.76	0.24
DEEP	1.04	0.18	1.18	0.19	1.22	0.26
DAP	0.85	0.18	1.25	0.18	0.81	0.26
DiPRP	0.93	0.18	0.49	0.14	1.17	0.24
DPRP	0.61	0.17	0.87	0.13	0.91	0.22
DIPP	0.84	0.16	1.00	0.10	1.27	0.19
BBP	1.29	0.13	0.36	0.07	1.19	0.15
DIBP	3.55	0.12	3.34	0.07	1.82	0.15
DBP	4.79	0.11	1.50	0.07	1.40	0.14
DBEP	1.33	0.12	0.66	0.06	0.41	0.14
DiAP	1.56	0.05	1.44	0.02	1.10	0.05
DPP	1.30	0.09	0.26	0.09	1.74	0.07
DCHP	1.51	0.04	0.75	0.02	0.56	0.05
BMPP	1.35	0.04	0.83	0.02	1.23	0.03
DHXP	1.24	0.04	0.66	0.02	1.57	0.02
DHP	1.86	0.04	0.99	0.03	1.45	0.02
DEHP	0.59	0.06	0.42	0.04	1.65	0.04
DNOP	1.76	0.08	0.85	0.06	0.98	0.06

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Table 2 Recovery of PAEs (n=6)

Compound	50 µg/kg		100 µg/kg	
	Measured Value	Recovery/%	Measured Value	Recovery/%
DMP	41.7	90.8	91.9	99.9
DMEP	47.9	104.1	101.3	110.2
DEP	44.5	96.6	100.7	109.5
DEEP	49.1	106.8	102.3	111.2
DAP	49.1	106.7	101.8	110.6
DiPRP	47.7	103.7	101.2	110.0
DPRP	48.4	105.2	105.0	114.2
DIPP	54.4	118.3	117.0	127.2
BBP	46.7	101.5	97.5	106.0
DIBP	45.4	98.6	97.7	106.1
DBP	47.8	103.8	100.8	109.6
DBEP	47.7	103.7	102.0	110.8
DiAP	36.0	78.2	77.0	83.7
DPP	45.7	99.4	90.8	98.7
DCHP	42.5	92.4	85.2	92.6
BMPP	45.3	98.5	90.7	98.6
DHXP	46.3	100.7	90.9	98.8
DHP	45.7	99.4	88.8	96.5
DEHP	46.0	99.9	96.9	105.4
DNOP	45.4	98.8	96.2	104.6

Conclusion

20 PAEs were separated by UHPLC in 14 minutes. The calibration curves of 20 PAEs were constructed over a concentration range of 5.0 - 200 µg/L with correlation coefficients (r) more than 0.999, respectively. Good reproducibility on both retention time (0.26% RSD) and peak area (4.79% RSD) was observed. The limit of quantity (LOQ) and the limit of detection (LOD) for 20 PAEs were based on the calibration curve of signal-to-noise ratio versus concentration. The method was established for fast quantitative determination of 20 PAEs in alcoholic drinks.

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