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Analysis of phthalate esters in environmental water samples by online-SPE-LC coupled with high-speed triple quadruple mass spectrometer

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Introduction

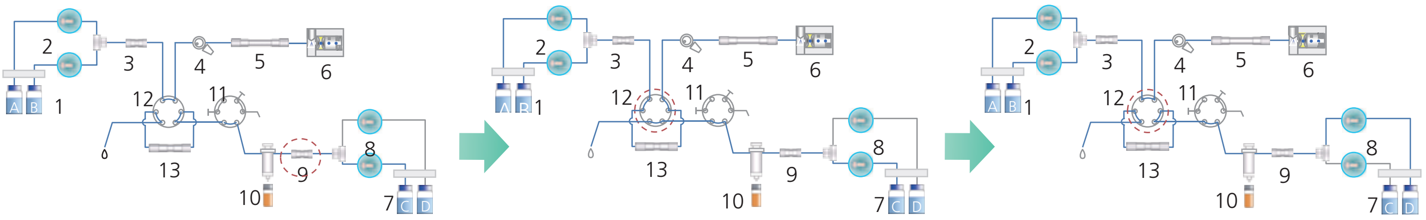
Phthalate esters are produced in large quantities throughout the world and used as primary plasticizers. These compounds, however, are of environmental concern due to their suspected endocrine disrupting potential. Furthermore, phthalate di-esters can be bio-transformed into mono-esters. Subsequently these compounds may be transported from wastewater to environmental water primarily due to insufficient wastewater treatment. Since both phthalate di- and mono-esters are likely to exist as a mixture in the environment, it is important to develop a simultaneous quantification method for both forms. In this study we developed a rapid online-SPE-LC system coupled with a high-speed triple quadrupole mass spectrometer for the simultaneous determination of phthalate di- and mono-esters to trace levels.

Materials & Methods

1) Sample loading

2) Elution

3) Analysis and wash SPE column



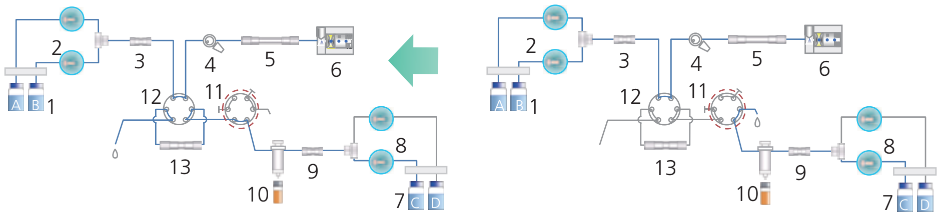
Sample was injected into SPE column by mobile phase C. Phthalate esters from the analytical system were trapped by scrubber column

Phthalate esters in samples was eluted by mobile phase for analysis.

Analysis of phthalate esters were performed and SPE column was washed simultaneously.

5) Equilibration of SPE column

4) Purge preparative mobile phase



Equilibration of SPE column was performed by mobile phase C.

At the starting of equilibration, the mobile phase was purged to avoid accumulation of phthalate esters on the SPE column.

1: Reservoirs for analysis
2: Pumps for analysis
3: Scrubber column
4: Manual Injector
5: Analytical column
6: LCMS-8030
7: Reservoirs for online-SPE
8: Pumps for online-SPE
9: Scrubber column
10: SIL-10AP with 5 mL syringe
11: Flow Change Valve (Purge)
12: Flow Change Valve (SPE)
13: SPE column

Fig. 2 Flow Diagram of online-SPE LCMS-8030 system.

Results

Development of analytical system.

High speed simultaneous analysis of phthalate esters was achieved by using high speed polarity switching (10msec) technology. Background contaminations were minimized with a scrubber column inserted after a mixing chamber.

Background peaks were however still detected with the scrubber column in place suggested that auto-sampler and valves can also a source of contamination for DBP, DEHP, DOP.

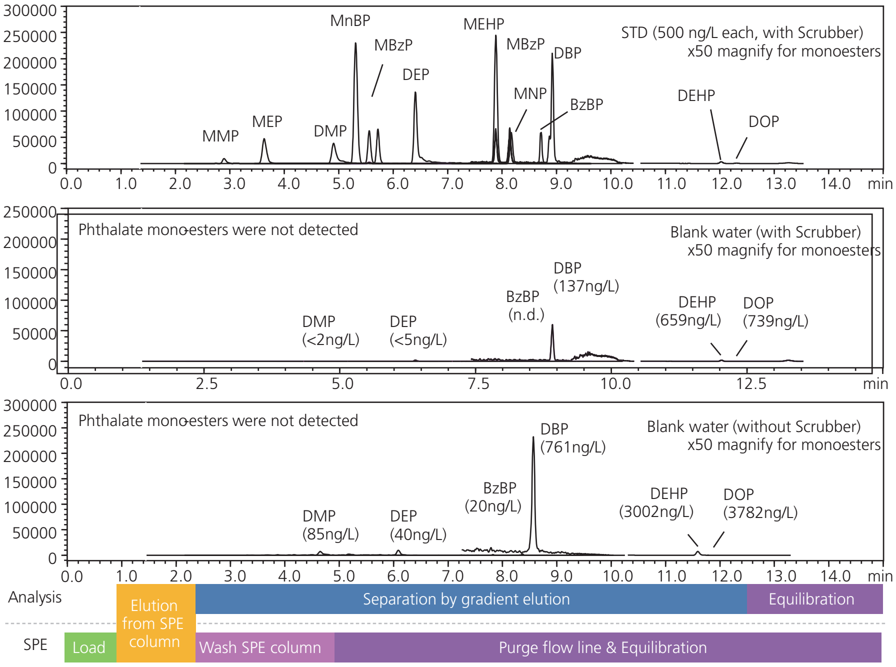


Fig. 2 Typical chromatogram of standard sample and blank samples.

Method performance characteristics in river water.

Compound	RT (min)	Recovery (%) at 500 ng/L*	Linear range (ng/L)	R^2	RSD (%) at LOQ
MMP	2.85	69.5 ± 11.6	100-10000	0.9997	9.3
MEP	3.65	103.6 ± 14.6	20-10000	0.9995	14.2
MEHHP	5.32	72.8 ± 0.1	10-10000	0.9996	13.0
MnBP	5.57	133.9 ± 16.1	10-10000	0.9991	11.1
MBzP	5.73	89.2 ± 3.5	5-10000	0.9974	12.7
MEHP	7.87	68.3 ± 12.7	5-10000	0.9994	8.5
MOP	8.12	53.3 ± 2	5-10000	0.9978	14.2
MNP	8.14	55.6 ± 12.6	5-10000	0.9987	17.8
DMP	4.95	97.4 ± 5.1	2-10000	0.9997	17.4
DEP	6.42	100.8 ± 17.8	5-10000	0.9991	8.4
DBP	8.92	101.1 ± 15.5	50-10000	0.9998	4.2
DEHP	12.04	105.3 ± 19.6	20-10000	0.9956	8.4
DOP	12.30	105.4 ± 4.7	20-10000	0.9966	7.2
BzBP	8.71	115.5 ± 9.8	5-10000	0.9994	19.7

$$*\text{Recovery}(\%) = \frac{\text{peak area of each components loaded by online - SPE (500 ng/L x 1 mL)}}{\text{peak area of each components loaded by manual injector (100 } \mu\text{g/L x 5 } \mu\text{L)}}$$

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LC conditions

Mobile phase A:	0.1% formic acid in water
Mobile phase B:	Acetonitrile
Scrubber column:	Shim-pack XR-ODSII (2 mm I.D. x 50 mmL., 2.2 µm)
Analytical column:	Shim-pack XR-ODSII (2 mm I.D. x 75 mmL., 2.2 µm)
Time program :	30%B(0-2.5 min)→98%B(10-12.5 min) →30%B(12.1-15 min)
Flow rate:	0.25 mL/min
Oven temp.:	40°C

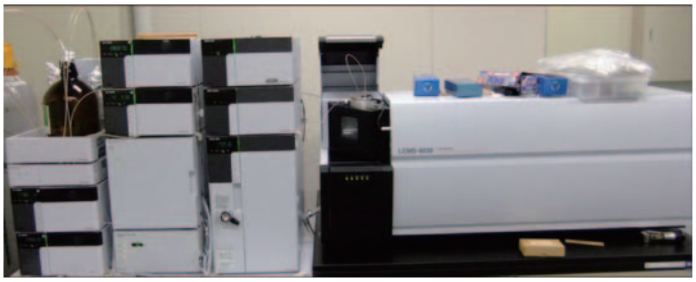
MS conditions

Ionization:	ESI pos./neg. polarity switching (pos. for di-esters, neg. for mono-esters)		
DL Temp.:	250°C	BH Temp:	400°C
Drying Gas:	10 L/min	Nebulize Gas:	2 L/min
Pause time:	3 msec	Polarity switching:	10msec

Monitoring ion, Collision energy, Dwelltime: See below

online-SPE condition

Mobile phase A:	0.1% formic acid in water
Mobile phase B:	Acetonitrile
Scrubber column:	Shim-pack XR-ODS (4.6 mm I.D. x 50 mmL., 2.2 µm)
Preparative column:	ENV-MASK (Purchased from Chemco Inc.) (2.0 mm I.D. x 10 mmL., 8 µm)
Flow rate:	2 mL/min
Injection vol.:	1000 µL



MRM parameters for target analytes

Compound name	Abbreviation	+/-	Q1 *m/z*	Q1 *m/z*	Q3 *m/z*	Dwell Time
Monomethylphthalate	MMP-N	-	179	11	77.3	200
Monomethylphthalate	MMP-IS	-	183	11	79.3	200
monoethylphthalate	MEP-N	-	193	19	77.3	50
monoethylphthalate	MEP-IS	-	197	19	79.3	50
monoethylhydroxyhexylphthalate	MEHHP-N	-	293	18	121.2	30
monoethylhydroxyhexylphthalate	MEHHP-IS	-	297	18	124.2	30
monobutylphthalate	MnBP-N	-	221	20	77.3	30
monobutylphthalate	MnBP-IS	-	225	20	79.3	30
monobenzylphthalate	MBzP-N	-	255	23	77.3	30
monobenzylphthalate	MBzP-IS	-	259	23	79.3	30
monoethylhexylphthalate	MEHP-N	-	277	14	134.3	30
monoethylhexylphthalate	MEHP-IS	-	281	14	137.3	30

Compound name	Abbreviation	+/-	Q1 *m/z*	Q1 *m/z*	Q3 *m/z*	Dwell Time
monooctylphthalate	MOP-N	-	277	26	77.3	30
monooctylphthalate	MOP-IS	-	281	26	79.3	30
monononylphthalate	MNP-N	-	291	19	141.3	30
monononylphthalate	MNP-IS	-	295	19	141.3	30
dimethylphthalate	DMP-N	+	195	-11	163.1	3
diethylphthalate	DEP-N	+	223.1	-20	149.05	3
dibutylphthalate	DBP-N	+	279.2	-17	149.05	3
dioctylphthalate	DOP-N	+	391.3	-23	149.05	50
diethylhexylphthalate	DEHP-N	+	391.3	-23	149.05	50
benzylbutylphthalate	BzBP-N	+	313.2	-25	91.1	3

Conclusions

- A novel simultaneous analysis method of phthalate di- and mono-esters combined with online-SPE was developed.
- The cycle time including online-SPE and column separation was 15 minutes.
- Background contamination from online-SPE and LCMS system were successfully minimized.
- Further method validation, including assessment of column life of SPE and recovery at several concentrations is underway.

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