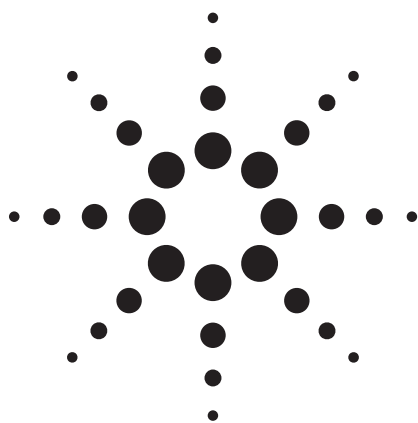


Determination of Sub-ppb Level of Phthalates in Water by Auto-SPME and GC-MS



Application

Environmental

Author

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Abstract

A solid-phase microextraction (SPME) method for the analysis of phthalates in water samples was developed on the CTC CombiPAL autosampler GC-MS platform. In this method, the sample preparation process was automated by using a CombiPAL autosampler, including the SPME fiber precondition, adsorption, and desorption, which improve the precision of the SPME method. The extraction temperature, extraction time, and salt-out effect are also studied. The optimized condition was applied to the analysis of real samples. The detection limits of the phthalates in this method are at the sub-ppb level.

Introduction

Phthalic acid esters (phthalates, PAEs) are key additives in many plastics to keep the plastics soft at room temperature. Because phthalates are not chemically but only physically bound to the plastic structure, the phthalates can leach from the plastic products. Due to their widespread use, relatively large amounts of these compounds are released into the environment. In recent years, considerable attention has been paid to human exposure to phthalates because of their suspected carcinogenic and estrogenic properties.

Liquid-liquid extraction (LLE) techniques have been widely used to isolate of PAEs from aqueous samples. These procedures are typically time-consuming, labor-intensive, and use a large amount of solvent. Solid-phase microextraction (SPME) is a fast, sensitive, solventless, and economical sample preparation method for gas chromatography analysis. The main advantages of SPME compared to solvent extraction are the reduction in solvent use, the combination of extraction and analysis into one step, and the ability to examine smaller sample sizes. It can also provide high sensitivity and can be used for polar and nonpolar analytes in a wide range of matrices with direct injection to both the gas chromatograph (GC) and the liquid chromatograph (LC).

Extraction of analytes from aqueous samples can be performed either by direct immersion of the fiber into the liquid phase or by headspace sampling. Adsorbed analytes are then thermally desorbed in the injection port of a GC and analyzed using an appropriate column and detector.

The CombiPAL provides a fully automated SPME sample preparation process. All movements of the SPME fiber from precondition, adsorption, and desorption are software controlled for optimum precision. Prior and during extraction, the samples can be shaken and heated. This approach dramatically reduces sample preparation time for semi-volatile compounds. Variable vial penetration depth allows compound extraction to be performed in liquid phase or in the headspace. After the compounds are thermally desorbed in the hot GC injector, the fiber may be regenerated in a heated and purged cleaning station.



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In this application, an automated SPME sample preparation process is demonstrated by using CombiPAL combined with GC-MS to determine plasticizers in a water sample.

Experimental

CombiPAL

Pre-incubation time:	60 s
Incubation temperature:	40 °C
Pre-inc. agitator speed:	500 rpm
Agitator on time:	5 s
Agitator off time:	2 s
Vial penetration:	25 mm
Extraction time:	1200 s
Desorb to:	GC Inj1
Injection penetration:	54 mm
Desorption time:	120 s
Post fiber condition time:	300 s

SPME

SPME fiber is from Supelco company (595 North Harrison Road Bellefonte, PA, USA), the fiber type is polydimethylsiloxane/divinylbenzene (PDMS/DVB) and the coating thickness is 65 µm.

6890 GC

Inlet temperature:	270 °C
Gas type:	Helium
Oven condition:	50 °C Ramps 10.00 °C /min to 260 °C (3.00 min)
Column:	DB-5ms 30 m × 250 µm, 0.25 µm
Mode:	Constant flow
Flow rate:	1.3 mL/min

5975 MS

Acquisition mode:	Synchronous SIM/scan
Mass range:	40–300
Sample:	3
Dwell time:	30 ms
MS source:	230 °C
MS quad:	150 °C

For other parameters, see Table 1.

The PAEs standards (shown in Table 1) were bought from Guo Yao Group (Shanghai, China).

The PAEs were dissolved in methanol at a concentration of 1,000 ng/mL and diluted by MilliQ water to the tested concentration.

Results and Discussion

Because PAEs are semivolatile compounds, immersion extraction mode was selected, and the sample volume was 18 mL.

Lots of unrelated peaks emerged in GC chromatograms when the extraction temperature was over 40 °C, which would shorten the lifetime of fiber, so a compromise has to be made between the lifetime of the extraction phase and the rate of equilibrium. We chose 40 °C for all extractions in the following experiments.

The effect of extraction time versus amount extracted at 40 °C was studied. The extraction efficiency for different compounds was proportional to extraction time. Figure 1 shows the profile of extraction time versus response. As seen in Figure 1, when the extraction time was over 20 minutes, the responses changed slightly, which means that the extraction of most compounds reached equilibrium at this point. In this experiment, 20 minutes was selected as the extraction time.

Salting-out effects by adding NaCl in the sample were also studied. The results showed that the extraction efficiency of DEP, DMP, and DBP was improved when salt was added, and that of DCHP, DEHP, and DPP (see compound names in Table 1) was decreased as shown in Figure 2. In this experiment, 20% (W/V) salt concentration was chosen. Figure 3 shows the SIM chromatogram of PAEs at the optimized condition. The chromatogram shows that improvements can be made to shorten the analysis time by adjusting the oven program.

Table 1. Compound Information

Compound name	Abbreviation	Retention time (min)	SIM ions
Phthalic acid, bis-n-pentyl ester	DPP	10.179	135, 149, 163, 177
Phthalic acid, bis-isononyl ester	DEHP	11.862	93, 105, 149, 177
Di-cyclohexyl phthalate	DCHP	15.749	93, 104, 149, 167
Diethyl phthalate	DEP	17.517	93, 105, 149, 177
Dimethyl phthalate	DMP	20.666	104, 135, 163, 194
Dibutyl phthalate	DBP	20.836	93, 149, 104, 205

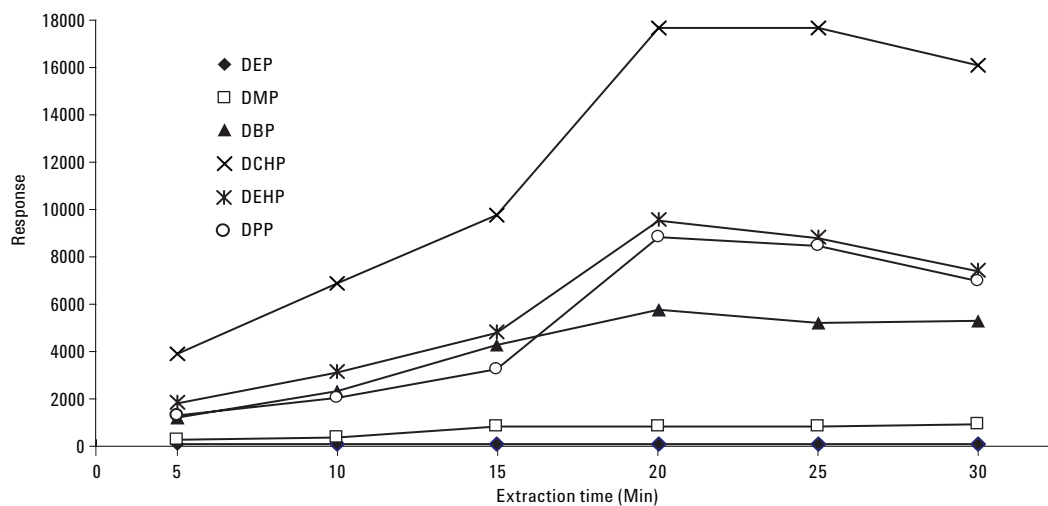


Figure 1. The profile of extraction time versus response (at 40 °C).

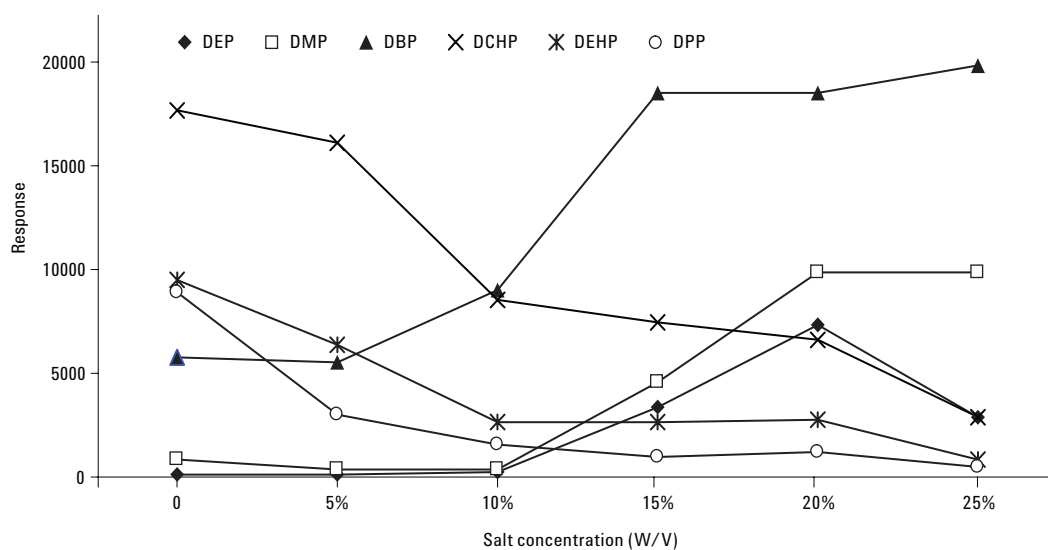


Figure 2. The effect of salt concentration on extraction.

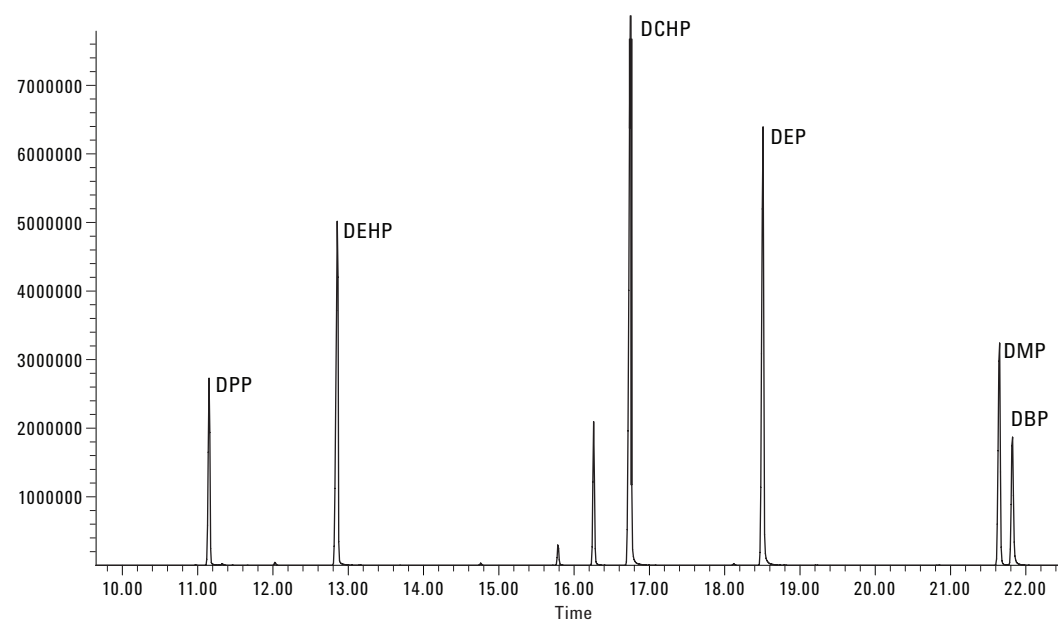


Figure 3. SIM of PAEs at the optimized extraction condition.

The linearity of the analytes was determined by calibration solutions with the concentration range from 0.5 ppb to 1 ppm at the optimized extraction condition. Table 2 shows the concentration ranges and correlating coefficients. The precision of the analysis, represented as relative standard deviations (RSDs) at 1 ppb, is also shown in Table 2. The RSDs for the organic esters are less than 10% except that of DPP; the detection limit is calculated at S/N of 3.

To demonstrate the performance of the optimized SPME method, tap water, potable water, and purified water from a water dispenser were analyzed for the phthalates' presence. Table 3 shows the phthalates detected in these three samples.

Conclusions

The CombiPAL autosampler with SPME is used for the analysis of PAEs in water. The precondition, extraction, adsorption, and desorption of SPME are automated and precisely controlled, which improves the precision of SPME method. Because the analytes concentrate into the coating of SPME, trace-level contaminants can be detected by using SPME. In this application, the detection limits for PAEs are down to sub-ppb level.

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Table 2. Method Validation Results

	Linear range (ng/mL)	Correlation coefficients (r^2)	RSD(%) N=7 (1 ppb)	Detection limits (ng/mL)
DPP	1–1000	0.996	12	0.34
DEHP	1–1000	0.996	8.6	0.29
DCHP	0.5–1000	0.989	8.9	0.08
DEP	1–1000	0.999	7.8	0.29
DMP	1–1000	0.998	7.1	0.38
DBP	1–1000	0.970	5.6	0.23

Table 3. Sample Analysis Results (quantitation unit = ng/mL)

	Tap water	Potable water	Purified water
DPP	n.d. ¹	n.d.	n.d.
DEHP	n.d.	n.d.	n.d.
DCHP	40.5	n.d.	n.d.
DEP	n.d.	78.9	n.d.
DMP	n.d.	23.6	n.d.
DBP	61.3	45.7	25.0

¹ None detected

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