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Determination of phenols by solid-phase microextraction

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Abstract

Solid-phase microextraction was investigated for the determination of phenols. Analytes were extracted by a thin layer of suitable sorbent coated on a fine fused-silica fiber. The fiber was then transferred into the injection port of a gas chromatograph, analytes were thermally desorbed and analyzed by gas chromatography. The best results were obtained with a polyacrylate coating by indirectly sampling in the head space above the liquid sample. The extraction period was 60 min, the desorption time was 8 min at 250°C. Acidification by hydrochloric acid (pH~1) and salting out (saturation by sodium chloride) were necessary for the best recovery.

Keywords: Extraction methods; Water analysis; Phenols; Nitrophenols; Chlorophenols

1. Introduction

The analytical determination of phenols is necessary because of their toxicity and their widespread use in industry. Contemporary methods of phenol analysis in water are mostly based on liquid–liquid extraction. These methods require complicated cleanup procedures with danger of analyte loss or contamination of sample. A number of these problems can be eliminated by the application of solid-phase extraction (SPE).

Solid-phase microextraction (SPME) is a fast, simple, sensitive and inexpensive technique, which does not require any organic solvents and can be simply automated. SPME employs distribution of an analyte between the liquid or gaseous sample and the stationary phase coated on fused-silica fiber. The fiber is then transferred into the injector of a gas chromatograph, where the analytes are thermally desorbed and separated by GC [1,2]. Direct connection of SPME to infrared [3] or Raman [4] spectroscopy is also possible. A special interface for the connection of SPME and HPLC has been also realized [5].

SPME has been successfully used for the determination of, e.g., volatile compounds in water [3,6,7], substituted benzenes (BTEX) [4,6], polyaromatic hydrocarbons (PAHs) [8], pesticides [9–11], phenols [12,13], amphetamine [14], polychlorinated biphenyls (PCBs) [8]. Besides aqueous matrices, more complicated samples have also been analyzed, e.g., soil, foods [15] and biological samples — especially blood [14] and urine [16].

2. Experimental

2.1. Instrumentation and reagents

A SPME fiber holder (Supelco Cat. No. 5-7330)

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with 85 μm polyacrylate (Cat. No. 5-7304) and 100 μm polydimethylsiloxane (Cat. No. 5-7300) fiber were used. A CHROM 4 gas chromatograph (Laboratorní přístroje, Prague, Czech Republic) with a DB-5 column (J&W, Cat. No. 320-1000); (30 m×0.53 mm, 1.5 μm) (80°C for 2 min, then 4°C/min to 250°C), a flame ionization detector (250°C) and helium (7 ml/min) (Linde, Technoplyn) as a carrier gas were used.

A standard phenol mixture EPA 604 M Supelco [phenol (0.5 mg), 2-chlorophenol (0.5 mg), 2-nitrophenol (0.5 mg), 2,4-dimethylphenol (0.5 mg), 2,4-dichlorophenol (0.5 mg), 4-chloro-3-methylphenol (2.5 mg), 2,4,6-trichlorophenol (1.5 mg), 2,4-dinitrophenol (1.5 mg), 4-nitrophenol (2.5 mg), 2-methyl-4,6-dinitrophenol (2.5 mg), pentachlorophenol (2.5 mg) in 1 ml of methanol] was used. A second standard phenol mixture contained phenol (20 mg), 2-methylphenol (20 mg), 3-methylphenol (20 mg), 2-nitrophenol (20 mg), 3,4-dimethylphenol (20 mg) in 1 ml of acetone.

According to the exposure time profile, 60 min as an extraction period and 8 min at 250°C as a desorption time were selected. For all experiments standard 30 ml EPA vial with 20 ml of water or 20 ml of 0.1 mol l^{-1} HCl saturated with NaCl (6 g/20 ml) was used. The sample was spiked by the standard phenol mixture on concentration level 0.5–2.5 μg ml^{-1}. For derivatization experiments 1 g of sodium bicarbonate ($NaHCO_3$) and 50 μl of acetic anhydride was added. The vial was quickly closed and immediately analyzed.

3. Results and discussion

3.1. Direct sampling

The efficiency of extraction was evaluated by distribution constants (K) [12]. The distribution constants for studied phenols on polyacrylate coating are shown in Table 1 for direct immersion, head space modification and head space modification with acidification and salting-out, respectively. The more effective extraction of 2-nitrophenol compared to 4-nitrophenol can be explained by hydrogen bond formation. While intramolecular hydrogen bonds in 2-nitrophenol decrease their solvation and solubility in water so enhancing their affinity to the coating, 4-nitrophenol forms intermolecular hydrogen bonds with the solvent which results in the decrease of the extraction yield.

The situation is more complicated in the series 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol. Solubility in water decreases with increasing number of halogens in the molecule. The observed efficiency decrease of 2,4,6-trichlorophenol in the neutral pH range can be explained by a positive mesomeric effect which spreads advantageously from positions 2,4,6 and effectively increases the electron density in the aromatic system and brings down the acidity of the phenolic proton. A negative induction effect, resulting from the high electronegativity of chlorine atoms, operates against the mesomeric effect and increases acidity. But the induction effect has a short range only, so it is

Table 1
Distribution constants of analyzed phenols on polyacrylate coating

	SPME	HS-SPME	HS-SPME NaCl. HCl
Phenol	23.94	8.60	81.33
2-Chlorophenol	143.31	109.62	1024.13
2-Nitrophenol	17.94	20.91	333.72
2,4-Dimethylphenol	177.22	25.76	595.91
2,4-Dichlorophenol	748.80	91.37	1604.43
4-Chloro-3-methylphenol	720.66	8.59	149.54
2,4,6-Trichlorophenol	135.59	31.80	1615.63
2,4-Dinitrophenol	129.48	3.62	14.83
4-Nitrophenol	3.80	5.44	7.18
2-Methyl-4,6-dinitrophenol	8.34	15.71	78.82
Pentachlorophenol	189.87	17.96	87.39

important only in the case of chlorine atoms in the positions 2 and 6. So induced acidity enhancement is more significant for the 2,4,6-trichlorophenol (both chlorine atoms in positions 2 and 6 are taking part in acidity increasing), than for the 2,4-dichlorophenol, where only chlorine atom in position 2 has a significant induction effect, while at position 4 the inductive effect is suppressed by the opposite mesomeric effect. It means, that in the series 2-chlorophenol (pK_a=8.48), 2,4-dichlorophenol (pK_a=7.89) and 2,4,6-trichlorophenol (pK_a=6.23) acidity is growing, but difference of dissociation constants (pK_a) of 2-chlorophenol and 2,4-dichlorophenol (0.59) is smaller than the difference of dissociation constants of 2,4-dichlorophenol and 2,4,6-trichlorophenol (1.66). At pH~1 dissociation is suppressed and distribution constants grow from 2-chlorophenol to 2,4,6-trichlorophenol.

3.2. Head space analysis (HS-SPME)

After immersion of the fiber to the stirring liquid sample a thin static layer is created at the surface of the fiber. This layer obstructs diffusion of the analyte molecules to the coating. This effect can be eliminated among others by indirectly sampling from the head space above the sample, because the diffusion coefficients of analytes in the vapor phase are about 4 orders of magnitude higher than in the aqueous phase [2]. Head space modification is also more sensitive because of the possibility of hard treatments of the sample such as acidification and salting-out. The possibility of analyzing specimens with solid particles and longer lifetime of fiber coating are also important preferences of head space modification.

Success of the head space technique depends on the transfer of analyte from the aqueous phase to the gaseous phase. Phenol and its derivatives are rather soluble in water and their equilibrium vapour pressure is relatively low, which negatively influences the possibility of determination by head space techniques. Suppression of dissociation of phenols by acidification and decreasing of solubility by salting-out leads to the improvement of the efficiency of the extraction (Table 1). For the best extraction a combination of both methods (acidification and salting-out) is necessary because salting-out decreases only solubility of electroneutral molecules, while acidification influences the dissociation equilibrium.

3.3. Derivatization

Derivatization of the polar phenolic –OH group is another way to decrease polarity of phenols and improve efficiency of extraction. But molecular mass increases during derivatization and it has negative impact on transport of analyte to the gaseous phase.

Derivatization by acetic anhydride is one of the most easy derivatization methods, because it does not require extraction by organic solvent before addition of reagent and acetic anhydride is well accessible in high purity. Although derivatization is more significant for adsorption on nonpolar phases (polydimethylsiloxane), it can have a positive effect on the more polar polyacrylate phase too, as can be shown in the case of 4-nitrophenol. Peak areas of free phenols and their acetates are compared in Fig. 1.

Derivatization has also chromatographic importance. Free phenols can interact with stationary phase or with material of injector chamber. After esterification of –OH groups they can be separated more efficiently [12].

3.4. Polydimethylsiloxane

Polydimethylsiloxane is one of the most extended phases for SPME today. Distribution constants on both phases (polyacrylate and polydimethylsiloxane)

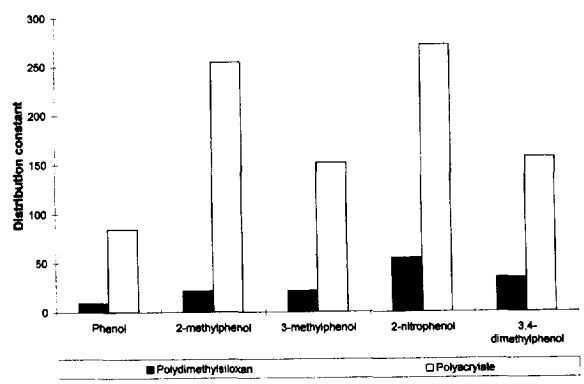

Fig. 1. Comparison of polydimethylsiloxane and polyacrylate coating (HS-SPME, salting out and acidification).

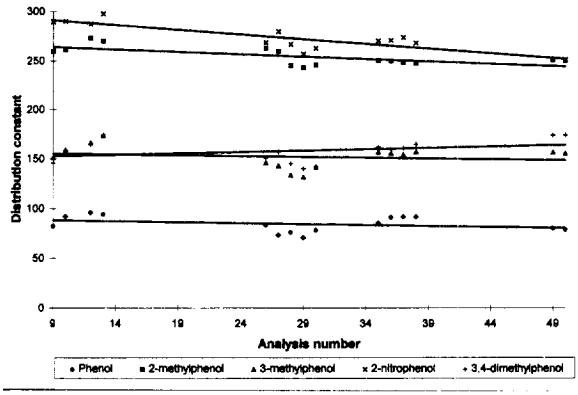

Fig. 2. Distribution constants dependence on number of analysis on polyacrylate coating (HS-SPME, NaCl, HCl).

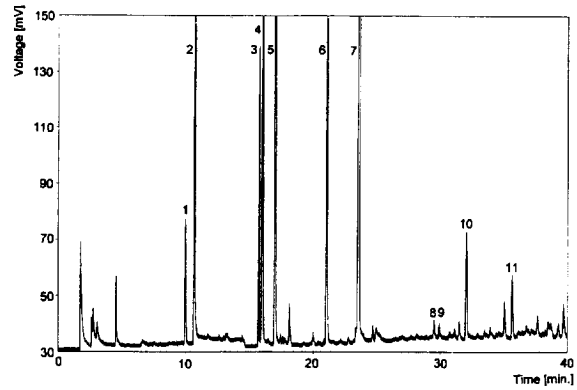

Fig. 3. Typical chromatogram of standard EPA 604 M Phenols Mix (1=phenol, 2=2-chlorophenol, 3=2-nitrophenol, 4=2,4-dimethylphenol, 5=2,4-dichlorophenol, 6=4-chloro-3-methylphenol, 7=2,4,6-trichlorophenol, 8=2,4-dinitrophenol, 9=4-nitrophenol, 10=2-methyl-4,6-dinitrophenol, 11=pentachlorophenol).

are compared in Fig. 2. These values were measured by the head space technique with acidification on pH~1 and saturation by sodium chloride. Fig. 2 shows, that polyacrylate gives about an order of magnitude higher recovery of free phenols than polydimethylsiloxane. The main limitation of polydimethylsiloxane for the extraction of phenols is the nonpolar character of the coating. The efficiency of extraction can be significantly increased by derivatization. So the selectivity of the extraction process can be influenced by the choice of stationary phase.

The state of matter of both phases is next important difference of solid polyacrylate from liquid, high viscous, polydimethylsiloxane. This has mainly impact on the kinetics of the whole process. While analyte molecules can diffuse through liquid polydimethylsiloxane film, diffusion in solid polyacrylate matrix is very difficult [12]. That is why such a long extraction period (60 min) was necessary for sufficient extraction.

3.5. Analysis reproducibility and coating lifetime

A coating lifetime is important for practical application (changes of efficiency with number of analysis). The coating is damaged mainly by a high temperature in the injection port of the gas chromatograph. The coating is also damaged during extraction, for example by irreversible adsorption or hydrolysis etc.

To study these effects a series of artificial samples was analyzed under the same conditions (concentration of each phenol: 1 μg ml^{-1}, sample volume: 20 ml, saturated by sodium chloride, pH~1, 25°C, extraction period 60 min by the head space technique). Very hard desorption conditions were chosen (8 min at 250°C) to maximize coating load and minimize carryover. Gains of extractions (like a distribution constants) are shown in Fig. 3 as a function of analysis number. These dependences confirm fiber lifetime guaranteed by the producer (50–100 analysis with one fiber). Excepting for 3,4-dimethylphenols a very slow efficiency decrease is visible. In the case of 3,4-dimethylphenol with two nonpolar methyl groups, the efficiency slightly increases with number of analysis. It can be explained by the increase in selectivity for nonpolar analytes during coating life. But the influence of these effects on analysis reproducibility is unimportant as is shown by the standard deviation values in Table 2. Linearity of calibration curves were verified in the range 0.1–10 mg l^{-1}. Fig. 4 shows typical chromatograms of standard EPA 604 M Phenols Mix.

4. Conclusion

SPME is a promising technique for the preconcentration of a wide spectrum of analytes. Experience shows the suitability of this method especially for

Table 2
Average distribution constants and standard deviations on polyacrylate coating (HS-SPME, NaCl, HCl)

	Distribution constants		
	Average	S.D.	R.S.D. (%)
Phenol	84.35	7.82	9.27
2-Methylphenol	254.78	8.78	3.45
3-Methylphenol	152.05	10.91	7.18
2-Nitrophenol	272.66	13.48	4.95
3,4-Dimethylphenol	158.11	11.12	7.03

screening analysis, for example in industry for waste waters, raw material or intermediates, for hygienic control or for monitoring of the environment.

For the determination of phenols without derivatization a more polar polyacrylate phase was used.

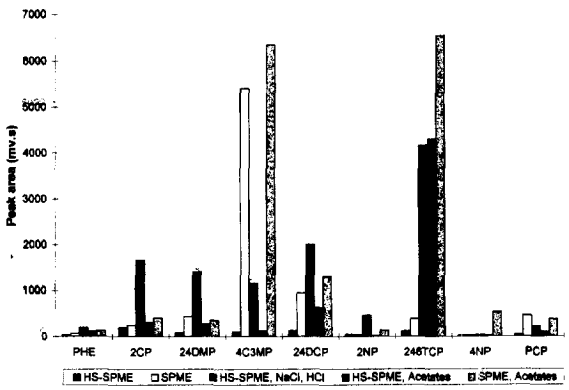

Fig. 4. Comparison of SPME techniques on polyacrylate coating (PHE=Phenol, 2CP=2-chlorophenol, 24DMP=2,4-dimethylphenol, 4C3MP=4-chloro-3-methylphenol, 24DCP=2,4-dichlorophenol, 2NP=2-nitrophenol, 246TCP=2,4,6-trichlorophenol, 4NP=4-nitrophenol, PCP=pentachlorophenol).

The best results were obtained by the head space technique at pH~1 (hydrochloric acid) with saturation by sodium chloride. A rather long extraction period (60 min) was used for successful extraction. A coating lifetime was sufficient for practical use.

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