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Short communication

Determination of phenols using simultaneous steam distillation–extraction

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Abstract

Simultaneous distillation–extraction was proposed as a preconcentration step for the determination of phenol and its derivatives in aqueous and soil samples. Detection limits of 0.01 mg l^{-1} (water) and 0.1 mg kg^{-1} (soil) were achieved by gas chromatography–flame ionization detection. The described preconcentration procedure was applied for the primary study of the adsorption equilibrium in a water–soil system serving as a model of phenol behaviors in the environment.

Keywords: Steam distillation–extraction; Soil; Extraction methods; Phenols

1. Introduction

Great attention has been paid to phenol analysis in environmental samples because of its widespread use in industry and high toxicological impact. The necessary preconcentration of phenol and its derivatives is commonly based on liquid extraction by suitable solvent (trichloromethane [1], dichloromethane [2], diethyl ether [3], benzene [4,5]). Nonpolar solvents (like a hexane) are suitable for the extraction of phenols after the derivatization (acetylation first of all) of polar, phenolic –OH group [6–9]. Solid-phase extraction (SPE) [10–13] and solid-phase microextraction (SPME) [14–16] eliminate the high consumption of hazardous, toxic and flammable solvents, emulsion formation and slow separation of layers, and, besides, can be easily automated. The extraction by alkaline aqueous solutions (0.1 *M* NaOH) [17–19] and supercritical fluid extraction (SFE) [20,21] were suggested for solid samples.

Simultaneous steam distillation–extraction (SDE) was originally used for analysis of food and agricultural products [22,23]: cheese [24,25], meal [26], dairy products [27] and so on. A microversion of the apparatus was used for water analyses. A wide range of organic pollutants, including ketones, aldehydes, alcohols, ethers, esters [28], fatty acids [29], phenols [30,31], aromatic hydrocarbons [26], nitrosoamines [32], polychlorinated biphenyls [33], triazine herbicides [33], were extracted from water samples.

2. Experimental

A J&W apparatus for SDE (Cat. No. 320-1000, Folsom, CA, USA) and a CHROM 5 gas chromato-

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graph (Laboratory Instrument, Prague, Czech Republic) were used. The DB-5 capillary column (30 m×0.53 mm I.D., 1.5 μm, J&W) with a flame ionization detection (FID) system (hydrogen at 30 ml min^{-1}, air at 250 ml min^{-1}, and nitrogen at 25 ml min^{-1} as makeup gas) and helium (flow-rate: 7 ml min^{-1}) as a carrier gas was operated at a temperature program of 100°C for 2 min to 250°C at 4°C min^{-1}.

All gases were purchased from Linde Technoplyn (Prague, Czech Republic). Dichloromethane, diethyl ether, acetone, sodium chloride, hydrochloric acid, sodium hydroxide, all of analytical grade, from Lachema (Brno, Czech Republic) were used. Phenol standards were obtained from Fluka (Buchs, Switzerland).

A 150-ml volume of aqueous sample, 60 g of NaCl, 7.5 ml of 2 mol l^{-1} HCl and two boiling chips were placed in the sample flask. Diethyl ether (10 ml) and two boiling chips were placed in the flask for the solvent. About 0.5 ml of diethyl ether was distilled to the central part of the apparatus. The temperatures of the oil bath with the sample and/or water bath with the solvent were adjusted to 160°C and/or 50°C, respectively, so boiling in both flasks began at the same time and extraction was carried out for 90 min. The extract was evaporated to 1 ml and analyzed by gas chromatography (GC) (injection 1 μl). The standard (100% recovery) was prepared by dilution of 400 μg of each phenol to 1 ml in diethyl ether.

For the soil analysis, 15 g dried soil was added to the sample flask under the same conditions (''reversible extraction''). For the next experiment (''irreversible extraction'') the soil (15 g) was extracted two times with 75 ml of 0.1 mol l^{-1} solution of sodium hydroxide for 30 min in an ultrasonic bath. The mixture was centrifuged, the supernatant was acidified by hydrochloric acid to pH~1, saturated by sodium chloride and extracted by the same way.

Soxhlet extraction was used as a comparative method [US Environmental Protection Agency (EPA) Methods 8040 and 3540] [34,35]. A 10-g amount of soil, spiked by 400 μg of each phenol, and 10 g of dry Na_2SO_4 were placed in the extraction cartridge and extracted by 300-ml dichloromethane for 20 h by four or five cycles per hour. The extract was evaporated in Kuderna Danish evaporator to 5 ml. Standard (100% recovery) was prepared by dilution of 400 μg of each phenol to 5 ml by dichloromethane. A 1-μl aliquot was used for each GC analysis. Real samples were proceeded by the same way.

3. Results and discussion

Recovery, defined as the ratio between the extracted and the given amount of the analyte, was used as a criterion of extraction efficiency. Thymol (2-isopropyl-5-methylphenol) was chosen as a surrogate standard for crosswise checking of raw data. Thymol is eluted earlier than commonly used 1-naphthol [30] and its determination is more reproducible. It was added after the extraction for the checking of the manual injection in the case of model samples. In real samples surrogate was applied before extraction to monitor the performance of the extraction. All data were processed with and without normalization on internal standard and no significant differences were observed. Conformity of both techniques served as a criterion of accuracy. Final data were calculated without normalization.

Approximately constant recovery was observed between 30 and 180 min. Thus, 90 min was selected as a compromise between a too short (poor reproducibility due to high thermal inertia of the system) and a too long extraction period (time consumption), respectively. Similar conditions were suggested previously by Janda and Krijt [30].

Recoveries of tested compounds are summarized in Table 1. The smallest recovery of 2-nitrophenol in aqueous samples can be explained by the high solvation of both polar function groups, so the tendency to pass to the gaseous phase is very low. The intramolecular hydrogen bond, typical for *ortho* derivatives, can decrease polarity of the whole molecule, so that a higher recovery of 2-nitrophenol than the 3- and 4-isomers should be expected. Methyl derivatives (2,6-dimethylphenol, 2-methylphenol) are extracted more efficiently, although their boiling points are rather high. The observed recovery is a result of conflict between the low volatility and the poor solvation of nonpolar methyl groups displacing methylphenols from the aqueous phase. Surprisingly, high recoveries of chloro derivatives were observed. Hydrophobicity of

Table 1
Recoveries of simultaneous distillation–extraction (SDE) and Soxhlet extraction (SE) of some phenols from aqueous and soil samples

	SDE				SE	
	Water		Soil[a]		Soil	
	Recovery (%)	SD[b]	Recovery (%)	SD[b]	Recovery (%)	SD[c]
Phenol	91.8	4.5	73.3	6.9	50.2	6.4
2-Methylphenol	88.8	3.1	76.9	2.9	44.2	8.2
2,6-Dimethylphenol	87.1	4.2	58.3	5.9	15.3	4.7
2-Nitrophenol	74.8	4.0	57.5	7.8	37.6	5.4
4-Chlorophenol	94.1	3.5	80.4	3.8	47.4	4.3
2,4,6-Trichlorophenol	91.6	5.2	81.9	6.2	55.1	7.3

[a] Irreversible extraction.
[b] Three independent extractions followed by three parallel GC analyses of each extract ($n=9$).
[c] Two independent extractions followed by three parallel GC analyses of each extract ($n=6$).

chlorine atoms is one of the phenomena strongly enhancing extraction efficiency.

Because of poor accessibility to reference soil with certified phenol contents, the standard sample was prepared in our laboratory as follows. A sample of soil (15 g) was placed in a round-bottom flask with 150 ml water containing 400 μg of each phenol. The flask and control flask without soil were stored at laboratory temperature from 1 to 160 h. Flask volume was centrifuged after incubation and supernatant and precipitate were processed separately.

The recovery of blank extraction stayed approximately constant during incubation period (1–160 h). Thus, no sample loss caused, for example, by adsorption or volatilization occurs in this system.

Readily decreasing phenol concentrations in the

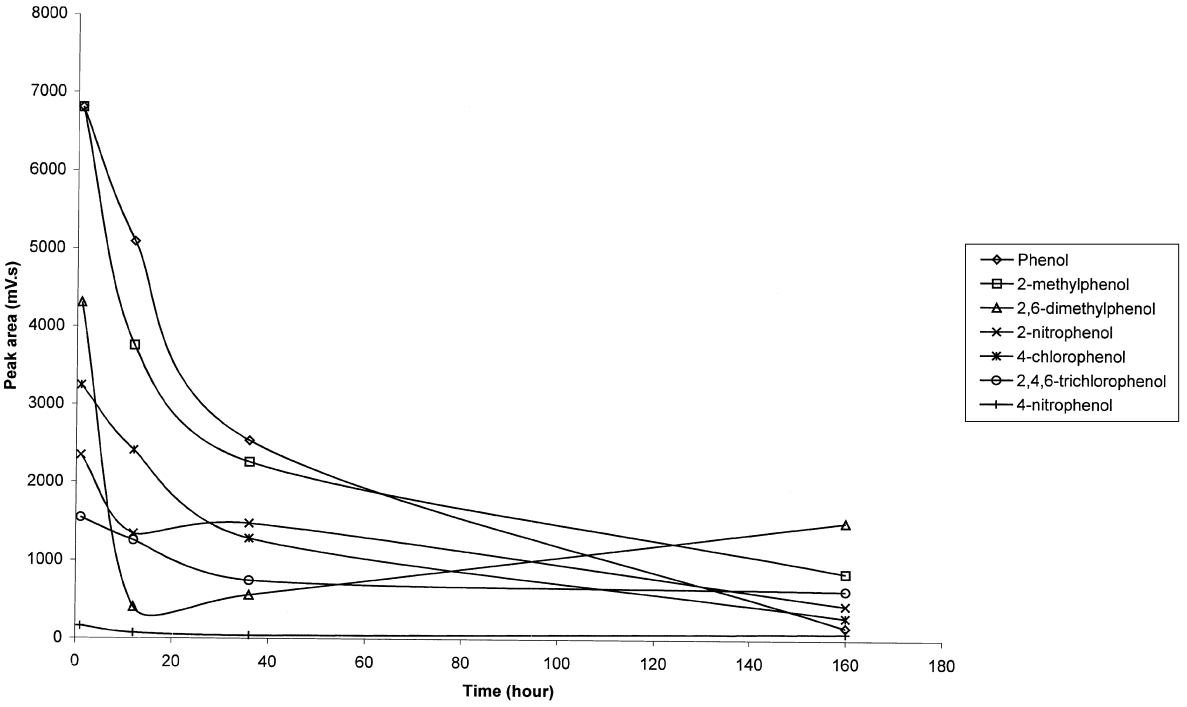

Fig. 1. Phenol amounts extracted by SDE from aqueous phase above the soil as a function of incubation time.

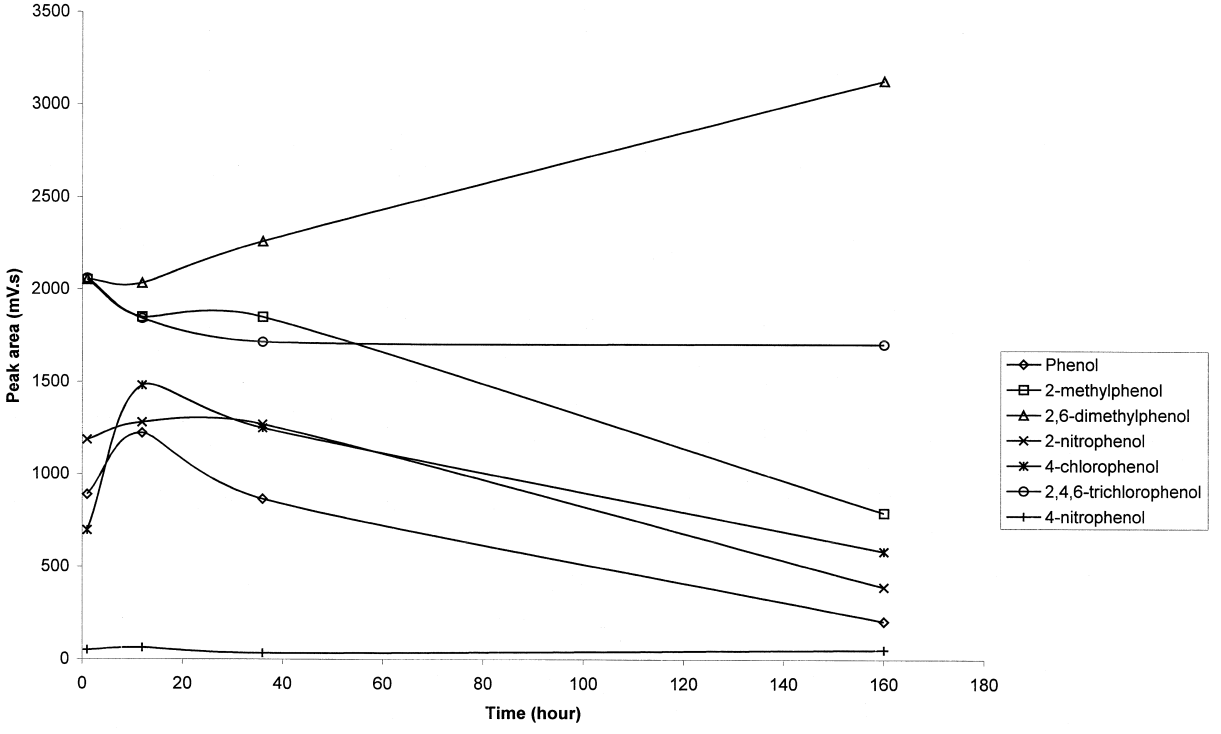

Fig. 2. Phenol amounts extracted by SDE from precipitate as a function of incubation time.

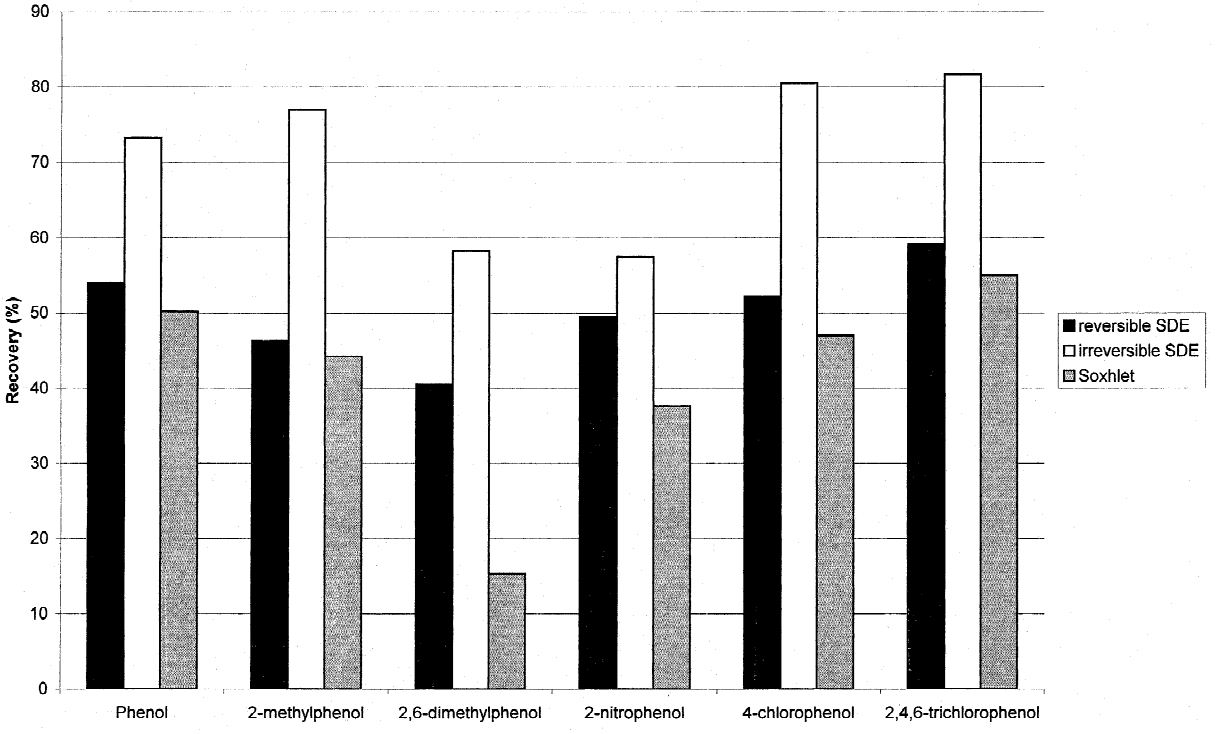

Fig. 3. Comparison of phenol recoveries from soils obtained by Soxhlet extraction, reversible and/or irreversible SDE.

water above soil was observed during the incubation period (Fig. 1). Phenols, lost from aqueous phase, must be present in the soil and analysis of the aqueous phase gives information about phenol concentrations in the soil. So, the precipitate can serve as standard soil with known amounts of phenols for evaluation of extraction efficiency.

The preliminary experiments with prepared soil were carried out in the same way as aqueous samples. So, 150 ml of distilled water was added to the precipitate, the mixture was acidified to pH~1, saturated by NaCl and extracted for 90 min. As can be seen from Fig. 2, extraction yields in soil do not change as much as could be expected according to Fig. 1. (Anomalous behavior of 2,6-dimethylphenol has not been explained yet).

The fact that extracted amount in the aqueous phase (Fig. 1) seems to be much more dependent on incubation period than soil ones (Fig. 2) suggests the view of slow irreversible adsorption. It can be considered, that the system simulates phenols behavior in the environment. A part of phenols from wastewater is quickly (in a few hours), reversibly adsorbed onto sediment. The residue undergoes slow

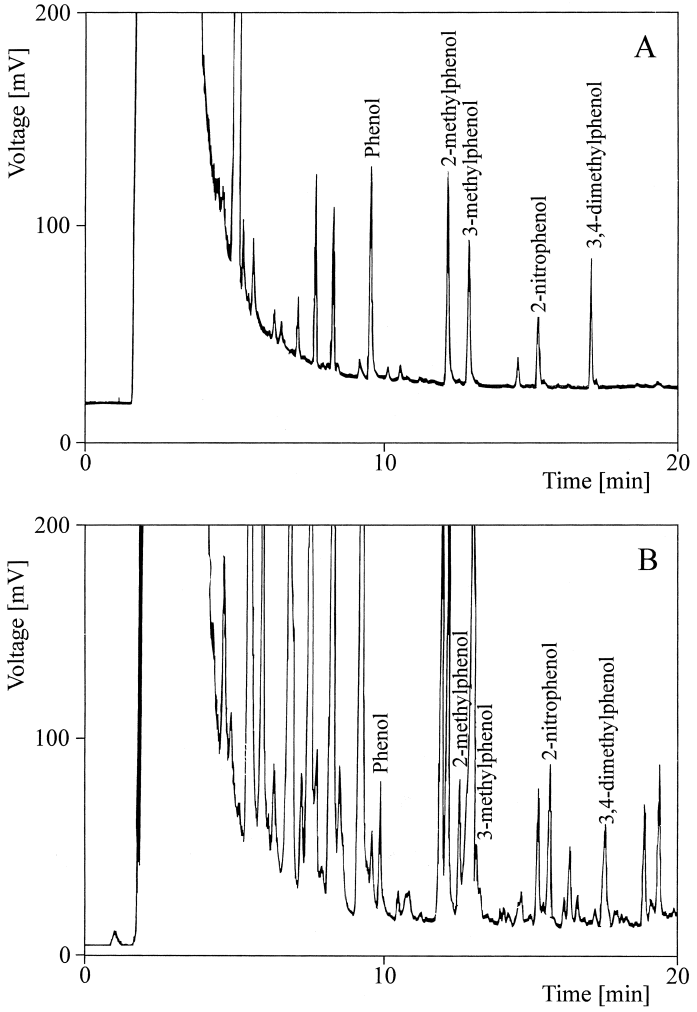

Fig. 4. Comparison of chromatograms obtained by SDE (A) and Soxhlet extraction (B).

irreversible adsorption during a few days. The described extraction procedure is able to determine reversible adsorbed phenols only.

For additional enhancement of extraction efficiency, extraction by 0.1 *M* NaOH in an ultrasonic bath was suggested. The precipitate was removed by centrifugation and the supernatant was extracted like a water sample. This procedure provides about 10–25% higher recoveries than the reversible system (Fig. 3).

The practical impact of the SDE procedure can be seen from comparison with standard methods for phenol analysis (Fig. 3). Soxhlet extraction in 300 ml dichloromethane for 20 h is prescribed by the standard US EPA methods for determination of phenols in soils [34,35]. Exemplary chromatograms of phenol extracts obtained by Soxhlet extraction and/or by SDE, respectively are shown in Fig. 4. Higher selectivity and higher extraction efficiency of SDE procedure are evident. Direct extraction leads to the recovery of non-volatiles which may cause interference during GC analysis after Soxhlet extraction. (An unidentified interfering compound was proved in the case of 2-nitrophenol by comparative analysis). A suitable cleanup procedure should be inserted between Soxhlet extraction and GC analysis, while the SDE procedure does not require any additional cleanup. Shorter extraction time and lower solvent consumption are other advantages of SDE.

4. Conclusion

SDE was suggested as a powerful tool for investigation of processes taking place in the environment contaminated by phenolic compounds. The detection limit of described preconcentration step in connection with GC–FID was estimated to be 0.01 mg l^{-1} and 0.1 mg kg^{-1} for aqueous and/or soil samples, respectively. Calibration graph linearity was verified in the range 0.2 to 30 mg l^{-1} and 0.2 to 300 mg kg^{-1} for aqueous and/or soil samples, respectively.

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