Accelerated Solvent Extraction of Phenols From Soil

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Accelerated solvent extraction (ASE) has been investigated as a method of sample preparation in environmental analysis. Using an experimental design approach the influence of operating variables (pressure, temperature and extraction time) on the recovery of seven phenols that have been slurry spiked on soil has been investigated. In every case, except 2-methylphenol, no variables were found to be significant within the limits investigated (pressure, 4–20 MPa; temperature, 30–70 °C; and extraction time, 5–25 min). ASE was compared with shake-flask extraction and found to give similar recoveries. The exception was 2,4-dimethylphenol which was not recovered by the shake-flask approach and was only poorly recovered using ASE (mean recovery, 24.5% with an RSD of 17.6%, based on 15 individual determinations). For shake-flask extraction the mean recoveries ranged from 70.3 to 116.1% with RSDs of 6.5 to 27.2% compared to ASE which gave mean recoveries from 73.8 to 90.2% and RSDs between 8.7 and 21.1%. It is expected that improvements in precision would be obtained using an automated ASE system. A cleaner UV chromatogram was obtained from the ASE extract. The feasibility of ASE in environmental analysis is demonstrated.

Phenolic compounds are toxic aryl alcohols widely used in the chemical industry for the manufacture of polymers, textiles, resins, dyes, petroleum refining, pulp processing and coal coking.[1–3] Moreover, chlorinated phenoxy acid herbicides and organophosporus pesticides can degrade yielding chloro and nitrophenols, respectively.[4–5] The determination of phenols in the environment is therefore indicative of industrial pollution. It is not surprising to find that some phenols are included in the list of priority pollutants of the US Environmental Protection Agency, as well as in some European regulations.[4,6] The analytical characterization of organic contaminants is the first step when considering an efficient strategy for soil remediation. Thus, due to their possible damaging effect on the environment, phenols must be monitored in a rapid and simple way. The sample preparation stage is crucial in any chemical analysis of environmental samples.

The analytical procedures applied for extracting phenols from the soil matrix prior to subsequent chromatographic analysis should avoid losses of the analytes and the use of large amounts of toxic solvents. As traditional methods, such as Soxhlet extraction, are time consuming and require large amounts of organic solvents, new alternative approaches are actively being sought. In this context both supercritical fluid extraction[7,8] and microwave-assisted extraction[9] have both been applied to the extraction of phenols from soils. This paper however, considers the use of accelerated solvent extraction (ASE)[10] for the extraction of phenols from soil. As ASE is the newest of the techniques available for extraction from solid matrices there is limited information currently available in the scientific literature. During the work reported in this paper a home-built system was utilized for extraction of seven phenols from a slurry-spiked soil sample.

Experimental

Instrumentation

A schematic diagram of the manual accelerated solvent extraction system is shown in Fig. 1. A syringe pump (Carlo Erba SFC 300, capacity 150 ml) was used to pump the organic solvent into the 2 ml stainless steel sample extraction cell (Phase Separations, Clwyd, UK) which was located in a fan controlled oven (temperature range 25–100 °C). A nitrogen cylinder, operated at 40 psi, was used to purge the sample of residual solvent. Strategic positioning of two Rheodyne valves allowed the extraction cell to be filled with solvent, isolated from the rest of the system or purged with either fresh solvent or N_2 gas.

The phenols were analysed using an isocratic HPLC system (Thermo Separations, Stone, Staffs, UK). An acetonitrile–water (40 : 60) mobile phase containing 1% acetic acid was pumped at 1 ml min^{-1} by a high pressure pump (model: P4000). Samples and standards were injected (50 µl) into a 25 cm × 4.6 mm ODS2 Spherisorb column (Phase Separations) located in a chromatographic oven maintained at 35 °C. Phenols were detected using a UV/VIS spectrophotometer (Model UV 1000) at 275 nm. Peak analysis was performed using Peak Simple software (SRI Instruments, Torrance, CA, USA).

Materials

Seven phenols were selected for analysis. Stock solutions of the phenols (phenol, 2,4-dichlorophenol, 4-nitrophenol, 4-chloro-3-methylphenol, 2-methylphenol, 2-nitrophenol and 2,4-dimethylphenol) were prepared at the approximate 1000 µg ml^{-1} level. All phenols were supplied by Merck, Poole, Dorset. Soil

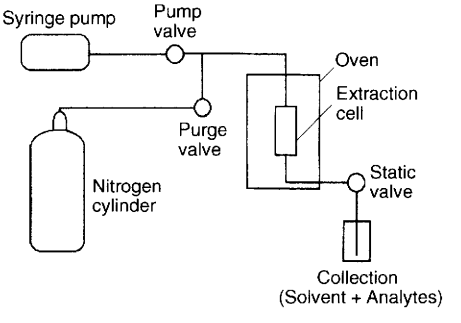

Fig. 1 Schematic diagram of manual ASE system.

(3.8% carbon, 3.4% water and pH of 6.1) was prepared after collection by air-drying and subsequent passing through a 2 mm sieve.

Procedure

Soil spiking

A sample of soil (15 g) was spiked using a slurry spiking procedure. Using this approach the phenols were added to a large volume of solvent (50 ml of acetonitrile) and the solvent evaporated overnight. In the absence of native samples, slurry spiking is the preferred approach.[11] Soil samples were spiked such that 100% recoveries were expected, on the basis of complete extraction, for each of the phenols. The concentration of phenols in the extractant solution was calculated to be 100 ng ml^{-1}.

Table 1 Experimental variables for the central composite design

	Pressure/MPa	Temperature/°C	Time/min
Star points	4 and 20	30 and 70	5 and 25
Mid point	12	50	15
Cube points	7 and 17	38 and 62	9 and 21

Accelerated solvent extraction

Approximately 0.01 g of Celite was placed at the outlet of the extraction cell prior to every extraction in order to prevent blockages. To the cell was then added about 0.5 g of the spiked soil sample. The cell was then placed in the oven at a preset temperature for 10 min to allow sample equilibration and the chosen pressure was applied for a period of time (5 to 25 min). Finally, the static valve was opened to allow fresh solvent to pass through the cell for about 10 s. A N_2 purge for removal of residual solvent was then applied. The volume of the extraction

Table 2 High-performance liquid chromatography performance data*

Compound	Retention time/min	%RSD	Capacity factor/*K*	%RSD
phenol	5.40	3.9	0.85	11.8
4-Nitrophenol	6.10	5.7	1.20	14.2
2-Methylphenol	7.08	6.1	1.53	13.1
2-Nitrophenol	9.06	6.8	2.24	12.5
2,4-Dimethylphenol	9.68	8.1	2.44	12.7
4-Chloro-3-methylphenol	11.19	9.7	3.02	14.2
2,4-Dichlorophenol	13.09	10.5	3.68	14.9

* n = 10 collected over five months.

Table 3 Central composite design results

Experiment number	Pressure/MPa	Temperature/°C	Extraction time/min	Percentage Recovery						
				Phenol	4-Nitrophenol	2-Methylphenol	2-Nitrophenol	2,4-Dimethylphenol	4-Chloro-3-methylphenol	2,4-Dichlorophenol
1	12	70	15	96	95	70	87	31	91	83
2	7	62	9	98	91	69	88	23	104	81
3	7	62	21	72	72	56	62	23	52	57
4	17	62	9	83	83	66	74	25	68	72
5	17	62	21	89	86	129	77	32	78	76
6	20	50	15	96	87	108	83	29	71	85
7	12	50	25	81	78	91	67	23	68	74
8	4	50	15	91	88	98	81	29	92	89
9	12	50	5	80	76	92	73	24	94	68
10	12	50	15	84	78	91	66	21	64	66
11	12	30	15	87	88	90	77	25	76	77
12	7	38	21	83	81	84	72	26	70	76
13	17	38	21	83	78	100	70	21	69	73
14	7	38	9	79	76	108	68	19	63	68
15	17	38	9	74	71	101	62	17	56	70

Table 4 Statistical data from multiple linear regression of the seven phenols

	Phenol	4-Nitrophenol	2-Methylphenol	2-Nitrophenol	2,4-Dimethylphenol	4-Chloro-3-methylphenol	2,4-Dichlorophenol
r	0.8524	0.8631	0.9404	0.8523	0.8085	0.8006	0.7192
r^2	0.7266	0.7450	0.8843	0.7264	0.6536	0.6410	0.5173
p-values—							
intercept	0.3850	0.1166	**0.0340**	0.1555	0.2456	0.5294	0.2962
P	0.2583	0.1959	**0.0255**	0.1251	0.1368	0.4186	0.1803
T	0.8376	0.4491	0.8101	0.5376	0.4425	0.9695	0.7515
t	0.2440	0.2524	**0.0435**	0.5608	0.7185	0.9559	0.5697
P^2	0.6329	0.5826	0.4408	0.2824	0.3898	0.7643	0.2516
T^2	0.7995	0.2519	0.2893	0.2699	0.4906	0.6525	0.5807
t^2	0.2559	0.3517	0.8805	0.7522	0.8142	0.7611	0.7840
PT	0.7216	0.4232	0.0663	0.6690	0.1558	0.9628	0.6888
Pt	0.0752	0.1791	**0.0060**	0.1316	0.7438	0.1283	0.4070
Tt	0.1085	0.1212	**0.0281**	0.1116	0.7438	0.1627	0.2685

solvent was approximately 10 ml. All extractions were done using acetonitrile only.

Shake-flask extraction

Approximately 1.0 g of soil was placed into a container and 10 ml of an acetonitrile–water (40:60) mixture added. The contents of the container were then shaken for 10 min and the liquid phase removed, filtered through a 0.2 μm filter (Acrodisc, Phase Separations) to remove particulates prior to analysis.

Experimental Design

An experimental design approach was used to evaluate the influence of the three main operating variables of ASE, *i.e.*, pressure, temperature and extraction time. The design chosen was a central composite design (CCD). In a CCD five levels of each variable are considered, and the number of experiments equals fifteen. The five variable-levels or values correspond to two star points, two cube points and one mid point. The limits of the variables or star points were set according to instrumental limitations. The ranges chosen were as follows: pressure 4–20 MPa (600–3000 psi); temperature 30–70 °C; and, extraction time 5–25 min. The CCD values are shown in Table 1.

Results and Discussion

HPLC Chromatographic Data

The retention time of the seven phenols studied over the course of this work (5 months) was determined. The results are shown in Table 2. The data shows the reasonable stability of the system. The approximate limit of detection of the seven phenols was as follows: 10–15 ng ml^{-1} for phenol, 4-nitrophenol, 2-methylphenol and 2-nitrophenol and 30 ng ml^{-1} for 2,4-dimethylphenol, 4-chloro-3-methylphenol and 2,4-dichlorophenol. Peak height was chosen as the method of quantitation for the chromatographic peaks as better precision was obtained (%RSD ranged from 4.0 to 21.4 for peak area measurements and 1.0 to 12.8 for peak height measurements, as determined over 2 d and based on 10 determinations). Calibration plots for each phenol were obtained over the concentration range 0–120 ng ml^{-1}. Correlation coefficients for the calibration plots ranged from 0.9990 to 0.9999.

Experimental Design

The fifteen experiments were done according to the CCD and the recoveries obtained are shown in Table 3. Multiple linear regression[12] was then applied to the data using a model of the following form:

$$Y = \beta_o + \beta_1 P + \beta_2 T + \beta_3 t + \beta_4 P^2 + \beta_5 T^2 + \beta_6 t^2 + \beta_7 PT + \beta_8 Pt + \beta_9 Tt$$

where Y is the percentage recovery of the individual phenol, β_o is the intercept, $\beta_{1...9}$ are derived coefficients, P = pressure, T = temperature and t is the extraction time. The results of the multiple linear regression are shown in Table 4. Significance at the 95% confidence level is indicated by a p value of <0.05. The significant values are highlighted in bold in Table 4. It can be seen that only 2-methylphenol has any significant variables at the 95% confidence level. The significant variables are the intercept, pressure and extraction time, together with the interaction terms of pressure × extraction time and temperature × extraction time. It is therefore apparent that the operating limits of the chosen variables have limited influence on the

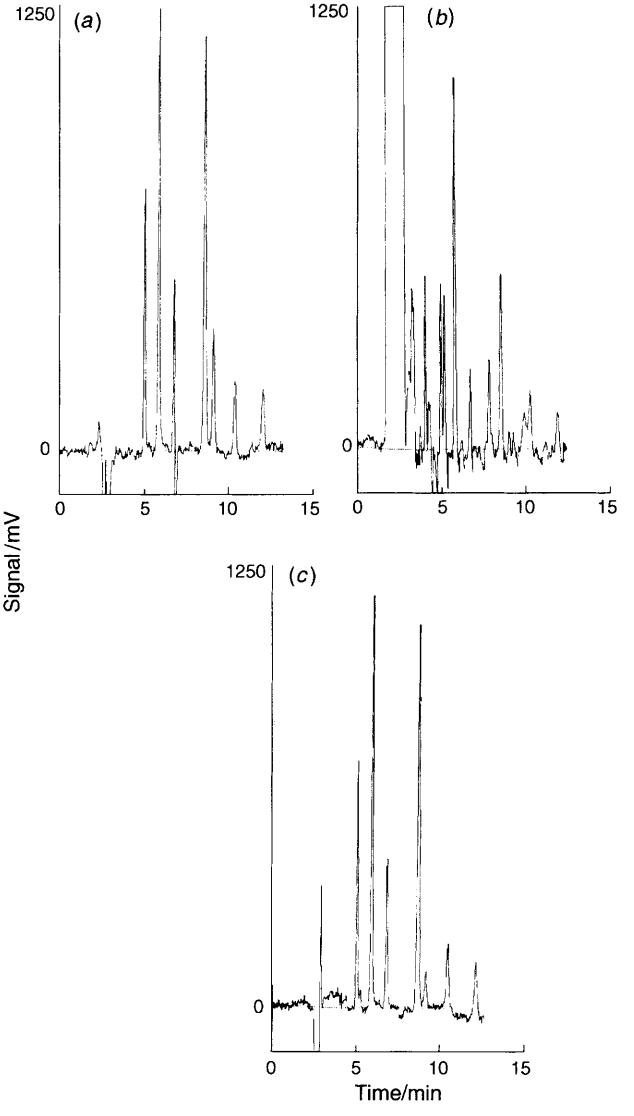

Fig. 2 HPLC chromatograms of (*a*) a 100 ng ml^{-1} phenol standard mixture; (*b*) shake-flask extract; and (*c*) accelerated solvent extract.

Table 5 Extraction of seven phenols from a slurry spiked soil: comparison of shake-flask and a manual accelerated solvent extraction

		Phenol	4-Nitro-phenol	2-Methyl-phenol	2-Nitro-phenol	2,4-Dimethyl-phenol	4-Chloro-3-methylphenol	2,4-Dichloro-phenol
Shake-flask*	mean	102.4	104.5	70.3	75.7	not recovered	116.1	88.2
	%RSD	6.5	8.1	15.1	27.2		17.9	19.6
	n	5	6	5	6	6	6	6
ASE†	mean	85.1	81.9	90.2	73.8	24.5	74.4	74.3
	%RSD	9.1	8.7	21.1	11.3	17.6	19.9	11.0
	n	15	15	15	15	15	15	15

* Acetonitrile–water (40:60). † 100% acetonitrile.

recovery of the phenols. The exception to this is 2,4-dimethylphenol which was only poorly recovered. As the limited recovery of 2,4-dimethylphenol was consistently low (< 32 %) it appears that some irreversible binding occurs to the soil matrix. The lack of dependence upon the operating variables of phenol extraction is shown in Table 5 where all fifteen sets of data are summarized in terms of percentage mean recovery and %RSD.

Comparison of ASE With Shake-flask Extraction

A comparison of shake-flask extraction and ASE was done to assess the potential of the newer technique. Using shake-flask extraction an acetonitrile–water (40 : 60) mixture was used for extraction. However, this was not possible with ASE. In ASE the presence of water caused blockage of the extraction cell by the soil–water suspension. All subsequent work using ASE used 100% acetonitrile. As can be seen in Table 5 similar recoveries were obtained using shake-flask, under the same conditions, as compared to the manual ASE method. It should be remembered that the ASE data is the mean of 15 experiments during which all three operating variables were altered. No recovery data was obtained for 2,4-dimethylphenol using shake-flask extraction. However, it was noted that the ASE method gave a cleaner HPLC chromatogram than shake-flask extraction (Fig. 2). The importance of this observation may lead to chromatographic column lifetime being extended.

Conclusions

Data presented demonstrates the potential for ASE in environmental analysis. The observed cleaner UV chromatograms obtained using ASE could have implications for column lifetime.

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