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# Optimization of preconcentration and isolation for the determination of 15 phenols by supercritical-fluid extraction and gas chromatography with metallomesogenic stationary phase

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## Abstract

Based on the merits of well-established capillary gas chromatography (GC), metallomesogenic polymer was used as the stationary phase and flame ionization detector (FID) was used as the detector, the analysis of phenolic compounds explored the possibility of application in complex matrices. We proposed the method combined supercritical-fluid extraction (SFE) of phenolic compounds, which had been enriched on the solid supports of XAD-4 resins, and then with their determinations by capillary GC-FID. The SFE parameters suitable for 15 phenols simultaneously adsorbed onto XAD-4 resins in aqueous solution were assessed by a $4^5$ factorial design method. The best results were 5 min static time, 10 min dynamic time, 0.25 ml methanol spiked, 80 °C oven temperature and 410 atm $CO_2$ pressure. Also, other parametric conditions for specific phenols were revealed and analyzed. In the comparison with Soxhlet extraction with regard to the recoveries and reproducibility, the developed SFE was quite superior and helped to reduce the detection limit of aqueous samples to $10^{-2}$-fold. Eventually, the polluted soils near a pharmaceutical factory were primarily tested and given the probable distribution.

*Keywords:* Phenols; XAD-4; SFE; Factorial design; Metallomesogen; Capillary; GC; Soil

## 1. Introduction

In a previous paper [1], we presented a GC-FID technique, in which capillary column was coated in the inner wall with columnar metallomesogenic polymers as the stationary phases. With unique selectivity for 15 phenols without further derivatization, the established method showed the calibration ranges and possible applications in complex matrices, such as effluent discharge into the water bodies and soils [2,3]. As many phenolic compounds and their conversion products with highly toxic character are hazardous to human health, the US Environmental Protection Agency regulated 11 phenols among the main environmental pollutants [4].

The success of solid-phase extraction is first determined by the proper choices of sorbents and desorption techniques. The adsorbing materials mainly include the reversed phase [5,6], anion exchanger [7,8] and graphitised carbon black [9] types. According to the study of 10 sorbents from Liska et al. [10], the styrene-divinylbenzene copolymer performed best, that is commonly considered as the result of the non-polar interactions between aromatic rings in both copolymer sorbent and phenols. Usually, when a strong sorbent is used, an effective desorption method may be followed.

Historically, Soxhlet extractions using organic–aqueous solvents at the boiling point were mostly used in the collection of residues in solid matrices, although this method consumes time and organic solvents. Nowadays, microwave-assisted extraction (MAE) [11], accelerated solvent extraction (ASE) [12] and supercritical-fluid extraction (SFE) [13–18] are developed to get better recoveries and reduce the drawbacks

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mentioned above. In addition to the effective extraction of polar and high-molecular mass phenols from soil samples within a short extraction time [19,20], SFE offers an environmentally friendlier choice among these pretreatments in the view of the using less amount of organic solvent.

Since many variables have to be considered simultaneously in SFE, factorial designs [13,17,18] and multilinear regression [21] both are formal optimization methods, excluding trial-and-error (univariate) procedure. In this study, we present a $4^5$ factorial design for optimizing SFE of styrene-divinylbenzene copolymer, XAD-4 sorbents, which are energetic and capable of the simultaneous preconcentration of 15 phenols in the diluted aqueous samples. The various polarities, which depend on the numbers and kinds ranging from alkyl to nitro substituents, are deeply concerned with the competition between phenols as to sorption, desorption and environmental impact. The individual SFE parameters for specific phenols as well as the optimal ones for all 15 phenols are suggested and approved. Real-world soils were primarily tested by our SFE/GC-FID system.

## 2. Experimental

### 2.1. Reagents and chemicals

Analytes including 2-chlorophenol, 2-nitrophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, 2,4,6-trichlorophenol, 3-methyl-4-chlorophenol, 4-bromophenol, pentachlorophenol (TCI, Tokyo, Japan), *o*-methylphenol, *m*-methylphenol, *p*-methylphenol (Wako, Japan), 4-nitrophenol, unsubstituted phenol (Merck, Darmstadt, Germany) and 2,4-dinitrophenol (Jassen, Belgium) were obtained from the indicated sources.

$CO_2$ supercritical fluid (Scott Speciality Gases, 99% purity) and methanol (Alps, ultra pure grade) were solvents used. The two sorbents, XAD-4 (20–60 mesh, average pore size 40 Å, surface area 725 $m^2/g$, Sigma, USA) and XAD-2 (infilling in solid phase extraction (SPE) cartridges, average pore size 90 Å, surface area 330 $m^2/g$, Alletech, USA) were made of polystyrene-divinylbenzene copolymer.

### 2.2. Apparatus

A Suprex SFE system (Model: Prep Master EL) was equipped with a reciprocating dual pump (ultimate 500 atm supply), an oven (ultimate 150 °C control), a six-port two position valve, a stainless steel vessel (5 ml capacity), and an automatic variable flow restrictor (stainless steel made, 10 cm length, 1/32 in. i.d., 1/16 in. o.d., 0.1–7.0 ml/min flow rate control, ultimate 100 °C control). To reduce the severe flux caused by mass expansion of the highly suppressed $CO_2$ fluid, the drain part of the SFE system was modified with a deactivated fused silica capillary (Polymicro, 25 cm × 50 μm i.d., 375 μm o.d.) as an extension to the steel restrictor. The capillary restrictor was wrapped in a heating tape to keep the fluid pressure at a moderate level release. The detailed construction was shown in reference [22] except that the SPE cartridge was filled with XAD-2 particles.

The gas chromatography used throughout for quantification of extract was a Shimadzu Model 17A, equipped with a split-injection system and an FID detector. The capillary column (15 m × 250 μm i.d., Restek, Bellefonte, PA) was dynamically wall-coated with synthetic metallomesogenic side-chain polymer, which beard copper carboxylato units in stacks [1]. Nitrogen was used as the carrier gas. Chromatograms were plotted on a Shimadzu CR-6A Chromatopac integrator.

### 2.3. Sample preparation

XAD-4 sorbents were treated with supersonic vibration in hydrochloric acid (6 M) for 30 min then stood for 2 h to get rid of inorganic impurity. After water rinsing, the sorbents were immersed in methanol for 3 h to dissolve organic impurity. Through rinsing by water then acetone, drying in vacuum oven at 80 °C and grinding into 60–100 mesh size, the treated XAD-4 sorbents were well prepared for the following two procedures.

The pretreated XAD-4 sorbent (0.3 g) and phenolic sample (2 ml, 15 phenols, each is 320 ppm in methanol) were both put in a glass bottle, which was capped after supersonic vibration for 1 min, and equilibrated statically for 3 days at room temperature. The utmost sorption of excess phenols by limited XAD-4 sorbents, which were received by gravitational filtration then air-drying in hood, was prepared for the SFE experiments of the factorial design. The samples for Soxhlet extraction compared with the SFE were prepared by the same procedure described above except 3 g pretreated XAD-4 and 8 ml phenols were used.

To evaluate the preconcentration ability of XAD-4 sorbents, the pretreated XAD-4 sorbent (0.5 g) and 10 aqueous samples, which were diluted from the $10^4$ ppm stock phenolic solution to 5, 1, 0.5, 0.2 and 0.1 ppm and made up 500 ml as well as 1000 ml, were tested through the above-described equilibrium balance as well as sorbent received and the following SFE procedures.

### 2.4. SF extraction

A four-level factorial design was employed to assess the significant five-factor (extraction temperature, extraction pressure, static extraction time, dynamic elution time and

Table 1
Factors on L16 factorial design

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| *A*; oven temperature (°C) | 50 | 80 | 110 | 140 |
| *B*; $CO_2$ pressure (atm) | 450 | 430 | 410 | 390 |
| *C*; static time (min) | 20 | 15 | 10 | 5 |
| *D*; dynamic time (min) | 25 | 20 | 15 | 10 |
| *E*; methanol spiked (ml) | 1.00 | 0.75 | 0.50 | 0.25 |

Table 2
Design matrix for L16 ($4^5$) factorial experiments

| Run | *A* | *B* | *C* | *D* | *E* |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 |
| 2 | 1 | 2 | 2 | 2 | 2 |
| 3 | 1 | 3 | 3 | 3 | 3 |
| 4 | 1 | 4 | 4 | 4 | 4 |
| 5 | 2 | 1 | 2 | 3 | 4 |
| 6 | 2 | 2 | 1 | 4 | 3 |
| 7 | 2 | 3 | 4 | 1 | 2 |
| 8 | 2 | 4 | 3 | 2 | 1 |
| 9 | 3 | 1 | 3 | 4 | 2 |
| 10 | 3 | 2 | 4 | 3 | 1 |
| 11 | 3 | 3 | 1 | 2 | 4 |
| 12 | 3 | 4 | 2 | 1 | 3 |
| 13 | 4 | 1 | 4 | 2 | 3 |
| 14 | 4 | 2 | 3 | 1 | 4 |
| 15 | 4 | 3 | 2 | 4 | 1 |
| 16 | 4 | 4 | 1 | 3 | 2 |

the volume of methanol modifier added directly to the solid samples) for optimizing SFE condition. The L16 orthogonal array tables (Tables 1 and 2) instructed the following 16 experiments in their individual parameters. For example, experiment no. 9 was assigned to the SFE parameters of 110 °C oven temperature, 450 atm $CO_2$ pressure, 10 min static time, 10 min dynamic time and 0.75 ml methanol spiked.

Irrespective of the SFE working conditions, all prepared samples, 0.2 g phenol-spiked XAD-4 or 1.0 g soil, were following the same procedure prior to SFE. In order to minimize potential interactions between the steel walls and chemicals in the samples, a piece of glass tubing (5 cm × 0.8 cm i.d.) with the sintered glass (100–150 mesh) cap at one opening was packed with sample, sealed with sufficient glass wool, and then placed in the extraction vessel.

A collection vial containing 1 ml methanol/$H_2O$ solution (volume ratio 1:1) was ready for the extracted and eluted analytes to trap in. As violent venting began, the evaporation loss was partially collected by SPE cartridge and flushed back into the collection vial by 0.5 ml collection solvent. After making up the collection solvent to 1 ml level, 1 μl extract was injected into the GC-FID system for recovery evaluation.

### 2.5. *Soxhlet extraction*

Three gram phenol-spiked XAD-4 was put in the cylindrical filter within Soxhlet extraction apparatus and extracted by 1:1 mixture (v/v) 100 ml of acetone and methylene chloride for 18 h at 80 °C [23]. Ten gram industrial site soil was mixed with 10 g $Na_2SO_4$ prior to the above procedure. The extracts were concentrated to 1.0 and 1.5 ml for phenol-spiked XAD-4 and soil samples, respectively, by vacuum distiller. One micro liter distillate was injected into the GC-FID system for recovery evaluation.

### 2.6. *GC analysis*

The well-established GC-FID system was very beneficial to separate 15 phenols well, especially for pairs of 4-bromophenol/3-methyl-4-chlorophenol/2,4,6-trichlorophenol without any tailing happening to highly polar groups and this was extensively discussed in reference [1]. Here, the optimal condition was set for 290 °C, injector temperature, 240 °C, FID temperature, 30 kPa, inlet pressure, 35, split ratio, and the temperature program followed as

Table 3
Obvious factorial factors and recoveries of substituted phenols from XAD-4 sorbents

| Substituted-phenols | Obvious factors in ranking[a] | Estimated SFE recoveries[b] | | Experimental recoveries[c] | |
|---|---|---|---|---|---|
| | | By individual obvious factors | By *A*2 *B*3 *C*4 *D*4 *E*4 | SFE[d] (% R.S.D.[e]) | Soxhlet (% R.S.D.[f]) |
| 2-Chloro- | *C*2 *A*2 *E*4 *D*4 *B*2 | 67.2 | 63.1 | 63.9 (9.5) | 46.3 (27.4) |
| 2-Nitro- | *C*2 *A*2 *E*4 *D*4 *B*2 | 88.5 | 82.9 | 90.5 (9.5) | 56.1 (23.5) |
| Unsubstituted | *C*4 *A*2 *E*4 *D*4 *B*3 | 51.6 | 51.6 | 48.9 (15.2) | 45.3 (26.8) |
| *o*-Methyl- | *C*4 *E*4 *A*2 *B*2 *D*4 | 71.2 | 71.0 | 65.8 (12.1) | 47.3 (23.9) |
| *m*-Methyl- | *C*4 *E*4 *A*2 *B*3 *D*4 | 67.3 | 67.3 | 64.0 (12.4) | 43.6 (21.5) |
| *p*-Methyl- | *C*4 *E*4 *A*2 *B*3 *D*3 | 86.5 | 86.3 | 82.1 (11.3) | 51.4 (24.6) |
| 2,4-Dimethyl- | *C*2 *E*4 *A*2 *B*3 *D*4 | 95.4 | 94.5 | 98.3 (10.3) | 63.9 (18.9) |
| 2,4,6-Trimethyl- | *D*4 *C*2 *E*4 *A*2 *B*3 | 84.3 | 83.6 | 87.9 (8.6) | 50.3 (26.9) |
| 2,4-Dichloro- | *C*2 *E*4 *A*2 *B*3 *D*4 | 85.3 | 83.4 | 84.2 (7.4) | 39.4 (25.5) |
| 4-Bromo- | *E*4 *C*4 *B*3 *A*3 *D*2 | 98.7 | 98.0 | 97.3 (7.2) | 43.8 (23.1) |
| 3-Methyl-4-chloro- | *C*4 *A*2 *D*4 *B*4 *E*4 | 98.8 | 98.4 | 98.5 (6.8) | 43.3 (20.2) |
| 2,4,6-Trichloro- | *C*4 *A*2 *E*4 *D*3 *B*2 | 97.4 | 95.2 | 98.6 (7.1) | 40.8 (17.8) |
| 2,4-Dinitro- | *C*4 *A*2 *B*4 *D*4 *E*4 | 99.2 | 98.9 | 98.9 (8.8) | 42.6 (18.5) |
| 4-Nitro- | *A*2 *C*4 *D*3 *B*2 *E*4 | 98.6 | 97.8 | 98.7 (8.4) | 43.5 (17.5) |
| Penta-chloro- | *C*2 *A*2 *E*4 *B*3 *D*4 | 95.7 | 95.5 | 95.8 (8.8) | 42.7 (17.6) |

[a] Determination from the evaluation of 16 experiments based on $4^5$ factorial design.

[b] Values, % units, calculated through $\Omega$ translation, $\Omega = 10\log[R/(1-R)]$, to avoid the estimated ones over 100%.

[c] Values, % units, calculated from the amount in extract ÷ the amount on sorbed XAD-4 × 100%.

[d] Condition under *A*2 *B*3 *C*4 *D*4 *E*4.

[e] Based on quintuplicate extractions.

[f] Based on triplicate extractions.

Table 4
Recoveries of phenols at low concentration in 500 and 1000 ml of reagent water with liquid–solid extraction using XAD-4 resins followed by SFE and GC-FID analysis

| Substituted-phenols | 500 ml | | | | | 1000 ml | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5.0 ppm | 1.0 ppm | 0.5 ppm | 0.2 ppm | 0.1 ppm | 5.0 ppm | 1.0 ppm | 0.5 ppm | 0.2 ppm | 0.1 ppm |
| 2-Chloro- | 55.8 (13.3)[a] | 68.8 (15.3) | 75.5 (15.4) | 80.5 (13.4) | 43.5 (14.8) | 53.6 (15.5) | 67.6 (14.8) | 67.3 (14.8) | 79.9 (14.2) | 46.5 (14.6) |
| 2-Nitro- | 65.0 (12.1) | 77.0 (15.0) | 88.4 (13.7) | 92.6 (13.5) | 53.3 (15.1) | 66.2 (16.2) | 72.0 (13.6) | 70.1 (14.5) | 74.6 (14.7) | 51.2 (15.3) |
| Unsubstituted | 28.7 (16.2) | 28.5 (16.1) | 30.1 (15.8) | 35.2 (15.1) | 25.6 (17.4) | 25.5 (17.7) | 25.4 (17.3) | 25.2 (17.0) | 31.0 (15.8) | 25.3 (16.4) |
| *o*-Methyl- | 68.0 (13.5) | 70.5 (15.5) | 78.9 (14.9) | 83.0 (14.5) | 53.8 (16.2) | 61.0 (14.5) | 63.2 (16.0) | 70.2 (16.1) | 81.6 (16.1) | 53.5 (15.5) |
| *m*-Methyl- | 75.2 (13.4) | 78.6 (13.4) | 86.0 (16.3) | 86.5 (13.7) | 54.6 (16.5) | 72.1 (15.0) | 71.8 (15.2) | 81.8 (15.3) | 85.3 (13.5) | 50.2 (15.0) |
| *p*-Methyl- | 80.0 (12.3) | 88.5 (14.1) | 90.7 (12.5) | 88.6 (12.4) | 60.5 (13.0) | 73.4 (13.8) | 86.3 (11.4) | 86.0 (12.2) | 85.9 (13.6) | 62.3 (14.3) |
| 2,4-Dimethyl- | 77.5 (11.6) | 88.4 (13.0) | 87.7 (13.4) | 93.5 (12.0) | 70.5 (14.7) | 70.8 (12.4) | 80.7 (13.3) | 79.5 (13.8) | 89.9 (11.1) | 68.5 (14.8) |
| 2,4,6-Trimethyl- | 81.1 (11.2) | 92.2 (11.3) | 95.5 (10.5) | 94.6 (10.5) | 70.6 (13.5) | 71.5 (11.2) | 84.3 (12.3) | 94.8 (11.4) | 89.6 (11.4) | 61.7 (15.1) |
| 2,4-Dichloro- | 91.6 (10.0) | 90.0 (12.4) | 91.0 (11.0) | 90.1 (11.3) | 72.0 (12.1) | 75.9 (11.8) | 86.1 (10.5) | 92.5 (10.6) | 84.2 (11.5) | 64.4 (13.7) |
| 4-Bromo- | 88.2 (10.6) | 92.2 (9.5) | 94.3 (10.8) | 94.0 (10.0) | 73.6 (12.4) | 81.0 (10.5) | 82.6 (9.6) | 92.3 (9.7) | 85.3 (12.3) | 66.5 (11.3) |
| 3-Methyl-4-chloro- | 81.1 (9.5) | 92.3 (10.3) | 93.5 (11.2) | 95.6 (9.6) | 78.0 (11.0) | 80.7 (11.5) | 86.9 (10.7) | 90.0 (9.7) | 90.0 (10.6) | 66.3 (12.4) |
| 2,4,6-Trichloro- | 89.0 (9.2) | 92.3 (9.3) | 89.4 (10.2) | 90.3 (9.2) | 79.9 (10.2) | 82.5 (10.3) | 84.5 (11.4) | 91.6 (10.0) | 91.0 (10.4) | 67.2 (11.6) |
| 2,4-Dinitro- | 84.1 (9.6) | 92.0 (9.8) | 94.0 (11.0) | 94.2 (9.1) | 81.7 (11.0) | 83.2 (9.6) | 89.1 (10.1) | 88.6 (9.4) | 89.9 (9.5) | 78.0 (10.3) |
| 4-Nitro- | 86.7 (8.9) | 91.8 (8.6) | 90.3 (10.2) | 93.5 (8.7) | 80.0 (10.6) | 86.6 (9.1) | 86.5 (9.6) | 93.5 (8.9) | 89.6 (9.4) | 74.2 (9.8) |
| Penta-chloro- | 88.6 (8.5) | 93.3 (9.7) | 93.8 (9.1) | 94.2 (8.4) | 82.6 (9.7) | 81.5 (9.7) | 91.0 (8.6) | 92.6 (8.7) | 88.8 (9.4) | 72.2 (9.8) |

[a] R.S.D. (%) based on triplicate experiments.

45 °C (5 min) to 85 °C (1 min) at 2 °C/min, then to 180 °C at 7 °C/min.

## 3. Results and discussion

### 3.1. Factorial experiments

According to the $4^5$ factorial experiments, which had been considered, the simultaneous effect within XAD-4 matrix and many phenolic competitors, individual optimal SFE conditions for 15 phenols were obtained, listed in Table 3, and ranked as their importance by the variance analysis of 16 experimental recoveries. We also listed the estimated highest recoveries for the individual under its optimal condition and the ones under the compromising condition, *A*2 *B*3 *C*4 *D*4 *E*4, whose factorial level was the most accepted in the list and supposed to be suitable for most phenols. Although the compromising recovery must be lower than the highest one for all phenols, the difference was less than 2.5% except 2-chlorophenol (4.1%) and 2-nitrophenol (5.6%).

Through a proceeding examination, the success in the factorial design was confirmed as the experimental recoveries under the compromising condition approached to the estimated ones. The differences were within ±4%, with the exception of 7.6% (2-nitrophenol) and −5.2% (*o*-methylphenol), and very desirable especially for the less volatile phenols. Our SFE processes were not only superior to Soxhlet extraction in the concern of recoveries and their R.S.D. values, but also comparable to other studies [13–18] although their interests were just limited in some categories and based on different sorbent matrices.

By checking the first obvious factors in the ranking, we found *C* factor, static equilibrium time, was the most popular and effective. More polar substituted phenols, such as nitro- and chloro-substituents, more times needed to be dissolved in SF from XAD-4 matrix. They could be also divided to two distinct groups, which were dominated by *C*2 (15 min) or *C*4 (5 min).

Factorial levels of *A* factor (oven temperature) appeared more consistent (i.e. *A*2, 80 °C) and dominant in the ranking list than *B* factor ($CO_2$ pressure), which level ranged from *B*2 (430 atm) to *B*4 (390 atm) to adjust SF density and then solubility of various phenols. XAD-4 matrix effect was actually responsible for the oven temperature control at 80 °C to thermodynamically overcome the desorption barrier in our system, which seemed reasonable when compared to the results of 50 °C/alkylphenols/soil [14], 90 °C/cresols/soil [17], 90 °C/cresols, chlorophenols/C-18 [16], 100 °C/chlorophenols/soil [13], 110 °C/phenol/PVC [18] and 120 °C/pentachlorophenol/wood [15] (p.s. SF temperature/phenols extracted/matrix).

*D*4 (dynamic time, 10 min) was the most favorite and economic among the four levels, if not, the loss of analyte in the collection vial would expand as dynamic purging time increased. *E*4 (methanol modifier, 0.25 ml) was the only choice, no matter what phenolic compound was observed. This implied that much methanol might be added so as to be the determinant factor for some cresols, which are relatively less polar.

### 3.2. Aqueous samples

Fifteen phenols containing in 500 and 1000 ml samples with five diluted concentrations were collected in 0.5 g XAD-4 resins and then extracted by SF under the compromising optimal parameters, *A*2 *B*3 *C*4 *D*4 *E*4. The recoveries were obtained from the SF extracts analysis by the installed GC-FID system and showed in Table 4. For most phenols, the best recoveries were found in the 500 ml, 0.2 ppm diluted sample. In fact, the recoveries would reach 80–95% for all phenols tested here except for the unsubstituted phenol (35%). This

Table 5
Comparison of recoveries between Soxhlet extraction and SFE on polluted soils

| Substituted-phenols | Concentration (ppm) in extracts[a] | | Concentraction ($\mu$g/g) in soils[e] | |
|---|---|---|---|---|
| | Soxhlet (% R.S.D.[c]) | SFE[b] (%R.S.D.[d]) | Soxhlet | SFE |
| 2-Chloro- | 54.8 (31.2) | 13.5 (10.5) | 17.8 | 21.1 |
| 2-Nitro- | 79.5 (26.5) | 20.8 (9.5) | 21.2 | 23.0 |
| Unsubstituted | 96.2 (32.2) | 17.6 (11.6) | 31.9 | 36.0 |
| *o*-Methyl- | 40.1 (25.7) | 5.1 (10.8) | 12.7 | 7.8 |
| *m*-Methyl- | 22.4 (26.2) | 5.8 (8.2) | 7.7 | 9.0 |
| *p*-Methyl- | 21.7 (25.9) | 5.1 (9.3) | 6.4 | 6.2 |
| 2,4-Dimethyl- | 39.8 (23.5) | 6.4 (10.1) | 9.3 | 6.5 |
| 2,4,6-Trimethyl- | 38.7 (29.4) | 7.7 (7.5) | 11.6 | 8.8 |
| 2,4-Dichloro- | 124.9 (28.5) | 43.3 (8.2) | 47.6 | 51.4 |
| 2,4,6-Trichloro- | 88.6 (25.1) | 32.0 (7.4) | 31.2 | 32.5 |

[a] Obtained from standard addition to the extracts.
[b] Condition under *A*2 *B*3 *C*4 *D*4 *E*4.
[c] Based on triplicate extractions.
[d] Based on quintuplicate extractions.
[e] Estimation based on the results of XAD-4 sorbents in Table 4.

phenomenon of getting low recovery for the unsubstituted phenol could be derived from the same problem showed in Table 3. The non-ideal recovery loss and R.S.D. values may be greatly caused from the procedures of the drying of wet XAD-4 after preconcentration and the violent purging during extraction collection. These deviations in off-line procedures would be especially found in those phenols with high volatility. However by the XAD-4/SFE treatment, the detection limit had been reduced to 0.2 ppm that was comparable to the one of 20 ppm in previously installed GC-FID system without sample derivation [1].

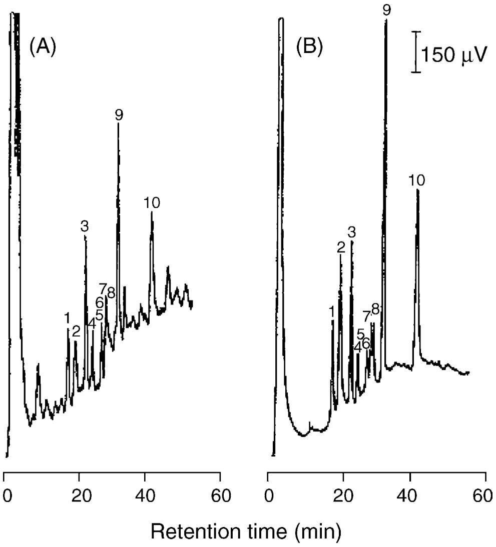

Fig. 1. Gas chromatograms of extracts in the Soxhlet extraction and SFE from polluted soil. (A) Soxhlet extraction; (B) SFE. Stationary phase: wall-coated capillary column (P-LCuSt, 15 m × 0.25 mm i.d.) [25]; injection volume: 1 ml; injector temperature: 290 °C; FID temperature: 240 °C; inlet pressure: 30 kPa; split ratio: 35; oven temperature: 45 °C (5 min) to (2 °C/min) 85 °C (1 min), then to (7 °C/min) 180 °C. Peak i.d.: (1) 2-chlorophenol; (2) 2-nitrophenol; (3) phenol; (4) *o*-methylphenol; (5) *m*-methylphenol; (6) *p*-methylphenol; (7) 2,4-dimethylphenol; (8) 2,4,6-trimethylphenol; (9) 2,4-dichlorophenol; (10) 2,4,6-trichlorophenol.

### 3.3. *Real-world soil samples*

In the comparison with XAD-4 sorbent, the sorption strength of effluent phenols onto soils, which may have many different chemical and textural characteristics, is also strong but more complicated. In spite of the consideration of solid matrix effect on the analytes, like spiking phenols onto certified soils [13,17], most studies pay little attention to the liquid matrix effects, such as whether the competing analytes are the adequate representatives of real pollutants as well as their aging products. We applied our established SFE and GC-FID systems, which were simultaneously aimed at 15 phenols, to analyze the polluted soils near a pharmaceutical factory.

The chromatogram in Fig. 1 revealed that SFE demonstrated its advantage over Soxhlet extraction, which was less selective so that its chromatogram was more indistinct and appeared some unidentified peaks. It also indicated that the constituents of extracts from SFE were relatively simpler and mainly included methyl- and chloro-substituted phenols, which may be products of microbial action and photodegradation from original pollutants of phenolic derivatives. The chromatographic result was nearly the same if the modifier was replaced with acetone.

These phenolic concentrations in Table 5 would be inferred from the recoveries in XAD-4 sorbents, even though there were certain differences between native analytes in soils and spiked ones in XAD-4 matrices. However, it is a good start to estimate the probable distribution by once SF extraction and GC-FID analysis. If necessary, a factorial experimental design to modify SFE parameters for specific solid matrices could be run again just like XAD-4 did.

## 4. Conclusions

The simultaneous optimization of SFE of 15 phenols in XAD-4 sorbents was successful through the experiments of a $4^5$ factorial design and the well-established GC-FID system. By the variance analysis of recoveries, we found that the factor of static equilibrium time was crucial to the more polar phenols while the less polar ones were affected by the amount of methanol modifier. Under the strong influence of matrix on the sorbbed analytes, SF temperature played a more important role than the pressure did. The clean-up system of XAD-4/SFE/GC-FID for the preconcentration and isolation of phenols in aqueous as well as solid matrices proceeded and approved to be superior to Soxhlet extraction in the matter of recovery and selectivity when XAD-4 sorbents and polluted soils were evaluated.

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