ELSEVIER

Journal of Chromatography A, 774 (1997) 243–251

JOURNAL OF CHROMATOGRAPHY A

Evaluation of supercritical fluid extraction, microwave-assisted extraction and sonication in the determination of some phenolic compounds from various soil matrices

María P. Llompart[a], Rosa A. Lorenzo[a], Rafael Cela[a,*], Ken Li[b], Jacqueline M.R. Bélanger[b], J.R. Jocelyn Paré[b]

[a]*Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*

[b]*Environment Canada, Microwave-Assisted Processes Division, Environmental Technology Centre, Ottawa, Ontario K1A 0H3, Canada*

Abstract

Extraction methods using supercritical fluid extraction (SFE) and microwave-assisted process (MAP) techniques, with or without a one-step in situ derivatisation, were evaluated for the extraction of phenol, *o*-cresol, *m*-cresol and *p*-cresol from soils. Five artificially spiked soil matrices were prepared; three of them were prepared by adding various amounts of activated charcoal in order to increase the degree of analyte–matrix interaction. We also applied the methods to a real phenol contaminated soil with a high carbon content (18%). To provide a basis for comparison, all the soils were extracted using an US Environmental Protection Agency-approved sonication protocol. The extracts obtained were analyzed on a GC–MS system without any preliminary clean-up or concentration steps. The results showed that SFE and MAP are more efficient than sonication with at least twice the recovery in all the soils tested. MAP and MAP-derivatisation showed the best recoveries (>80%) for the five spiked matrices studied with the exception of *o*-cresol in soils with activated charcoal content higher than 5%. In these specific soils, SFE showed very low recoveries for the four phenols. However, recoveries were significantly improved when a derivatisation step was combined to SFE. In the real soil tested, the recoveries using derivatisation–extraction process were lower than the recoveries using extraction process. In general, derivatisation–extractions perform better and do not require extreme extraction conditions.

Keywords: Extraction methods; Soil; Derivatisation, GC; Phenols; Cresols

1. Introduction

Phenol and cresols are constituents of crude oil and coal tar. Also, phenol compounds are widely used in the chemical industry. It is well known that these compounds exhibit properties that are hazardous to human health [1,2], thus making it necessary to identify the occurrence and levels of contamination carefully in the environment, specially for soil reclamation.

It has been recognized that the automatization of the measurement and determination stages in the analytical process has been developed significantly over the past decades. On the contrary sample preparation automatization is comparatively much less developed. Much work has been carried out in the analysis of liquid samples [3]. However, solid or particulate samples represent a very important fraction in environmental studies. For these kind of

*Corresponding author.

PII S0021-9673(96)01025-4

samples an extraction step of the analytes of interest usually has to be carried out. The procedures involved in the extraction of phenols from soil samples (e.g., Soxhlet) are usually lengthy and non-selective. Moreover, they entail a great deal of sample handling, which adds to the risk of errors [4,5]. Recently, supercritical fluid extraction (SFE) and microwave-assisted processes (MAP) have become an important alternative for the extraction of organic pollutants from environmental matrices. Allowing unattended-simultaneous-extraction of several samples, it can be easily connected to the final separation and/or determination techniques thus rendering fully or mostly automatized analytical processes. These techniques offer a better control over the extraction conditions thus allowing for the extraction to be performed in relatively shorter times and more selectively. With generally less sample handling and "tuneable" extraction conditions, they provide relatively clean extracts and thus expedite sample preparation by eliminating further sample cleanup thus reducing the risk of errors and artifacts as well as the use of environmentally aggressive solvents [6–17]. Sample throughput with microwave extractors is usually higher than that obtainable by SFE [13–15]. Moreover, during SFE or MAP extraction, an in situ derivatisation step can be carried out by adding a derivatising reagent to the sample matrix [17–20]. Amongst the possible derivatisation procedures we note a simple an efficient acetylation of phenols by means of direct reaction with acetic anhydride. This in situ step yields extract with improved chromatographic characteristics with respect to the underivatised phenolic compounds.

On the other hand, it is clear that when dealing with sample preparation–automation schemes the sample has to play the capital role. Several reports to date deal with methods that have been optimised using only samples spiked with the analytes immediately prior to extraction [21]. This approach is limited by the fact that it does not reflect the complex and intricate nature of analyte–matrix interactions that develop and intensify over time [22]. Because of the restricted availability of certified reference materials for real contaminated samples, we made every reasonable effort to maximise analyte–matrix interactions so as to use a matrix as close as possible to a real world sample during the course of the method development work.

In this study, we directed our efforts toward evaluating two extraction and two extraction–derivatisation methods for the extraction of phenol and cresols from soils using SFE and MAP techniques that had been optimised previously by using factorial design approach [18,19,22–25]. For this purpose, we have prepared five different spiked soil matrices. In order to increase the degree of difficulty of the sample to be extracted, three of them were prepared by adding activated charcoal. The adsorption of phenol compounds in this kind of matrix is known to be very strong. We also applied the four methods to a real phenol contaminated soil with a high carbon content (18%). Finally, to provide a basis for comparison, all these soils were also extracted using an US Environmental Protection Agency (EPA)-approved sonication protocol [26].

2. Experimental

2.1. Microwave-assisted process extraction

MAP experiments were performed with a 950-W MES-1000 microwave sample preparation system (CEM Corp., Matthews, NC, USA). This extractor has provision for 12 simultaneous extractions. A 1-g aliquot of soil was accurately weighed into a PTFE-lined extraction vessel; acetone and hexane were added to each sample for the extraction experiments and 200 μl of pyridine, 800 μl of acetic anhydride and 9 ml of hexane for the extraction–derivatisation experiments. The extraction vessels were closed after ensuring that a new rupture membrane was used for each extraction. For this study, 4–6 simultaneous extractions were performed using full power. Extraction conditions are summarised in Table 1. At the end of the extraction program, the sample carrousel was removed from the microwave cavity and cooled in a water bath. The control vessel was returned to the microwave to check that the extract was at room temperature before opening. Solvent losses were checked in several randomly selected experiments and were found below 1%. Using a glass pipette, 1 ml of the clear supernatant was transferred to an auto liquid sampler injection vial. Any particulates in the raw extract were removed by a nylon syringe filter. An internal standard (1,4-dichlorobenzene) was

Table 1
MAP and MAP-derivatisation parameters and conditions

Factors	MAP	MAP-derivatisation
Extraction temperature (°C)	130	130
Quantity of pyridine (μl)	–	200
Quantity of acetic anhydride (μl)	–	800
Quantity of hexane (ml)	2	9
Quantity of acetone (ml)	8	–
Time for reaching the extraction temperature (min)	5	20
Extraction time (min)	10	5
Sample size (g)	1	1
No. of samples extracted simultaneously	4–6	4–6

added and the raw extract was analysed by GC–MS without any clean up or concentration procedure.

2.2. Supercritical fluid extraction

SFE experiments were performed on a Hewlett-Packard 7680T supercritical fluid extractor (Hewlett-Packard, Avondale, PA, USA), using standard cells of 7.0 ml inner volume. In order to minimise contamination and plugging of the sintered disks, the top and the bottom caps of the extraction cell were fitted with two filter paper disks of the same diameter as the cap I.D. A snugly-fitted piece of PTFE tubing having the same diameter as the cell I.D. was inserted into the extraction cell in order to minimise the interaction of the analytes with the metallic surface of the cell. The cell was first packed with a layer of Celite, followed by a weighed aliquot (ca. 1 g) of soil sample into which 100 μl methanol was added as a modifier. In extraction–derivatisation experiments, the modifier was substituted with the derivatisation reagents. The remaining void volume of the cell was packed with Celite. The end cap was secured and the cell was placed into the extraction chamber. Extraction conditions are summarised in Table 2. Upon the completion of extraction, the analytes were rinsed from an ODS (octadecyl siloxane) trap by two individual 1 ml aliquots of hexane. The second rinse of the ODS trap in all cases did not have detectable amount of the analytes and subsequently not collected. The volume of extract was determined by weighing; 1,4-dichlorbenzene was added as an internal standard prior to GC–MS analysis. Because the collection vials fit GC–MS autosampler sites the procedure can be considered fully automatized from the moment the sample is placed in the extraction chamber.

2.3. Sonication

Extraction using an ultrasonic probe (Braun-Sonic U 2000, 175 W) was performed using 2.5 g portions of soil. The sample was sonicated 3 times of 3 min each with 10 ml dichloromethane in continuous power mode. The raw extracts were combined and made to a 25-ml final volume. The extracts were analysed without any clean up or concentration steps. A 1-ml aliquot of the extract was transferred to the injection vial and after the addition of the internal standard (1,4-dichlorobenzene) the raw extract was analysed by GC–MS.

2.4. Reagents and chemicals

The phenol standards used were supplied by Aldrich (Milwaukee, WI, USA). Activated charcoal was obtained by Fluka (Buchs, Switzerland). Acetic anhydride was purchased from BDH (Poole, UK)

Table 2
SFE and SFE-derivatisation parameters and conditions

Factors	SFE	SFE-derivatisation
CO_2 density (g/ml)	0.77	0.4
CO_2 flow-rate (ml/min)	1.5	1.2
Extraction cell temperature (°C)	90	115
Nozzle temperature (°C)	45	45
Trap temperature (°C)	20	20
Static extraction time (min)	10	5
Dynamic extraction time (min)	15	15
Amount of pyridine (μl)	–	20
Amount of acetic anhydride (μl)	–	115
Amount of methanol (μl)	100	–

and pyridine, methanol, *n*-hexane, acetone and dichloromethane from Caledon (Ottawa, Canada). The phenol stock solutions were prepared by weighing an appropriate amount of the standard and dissolved in 10 ml hexane. Working solutions were made by appropriate dilution of the stocks. All the solutions were stored at 5°C in the dark. For quantitative gas chromatography determinations, calibration was carried out at four concentration levels spanning the range 50–2000 ng/ml. To derivatise the standard solutions, 20 μl pyridine and 50 μl of acetic anhydride were added to 0.93 ml of the phenols standard solution. Solutions were thermostated at 80°C for 30 min prior to analysis on the chromatograph.

2.5. Preparation of spiked soil matrices

A garden soil sample was obtained from Campus of Santiago de Compostela (Santiago de Compostela, Spain). The carbon content was found to be 2.2%. From this soil, three additional soil matrices were prepared with 2, 5, 10% (w/w) activated charcoal contents. An industrial lignite mining soil (Endesa soil) was obtained from the slag of the Power Station of "Puentes de Garcia Rodriguez" (La Coruña, Spain) with a carbon content 7.2%.

Each soil was dried in an oven at 105°C for 48 h, ground and sifted to a particle size below 300 μm. A 100-g aliquot was slurried with 100 ml of a methanolic solution of phenols. The sample was then allowed to air-dry with occasional stirring at ambient temperature, protected from draught for 5 days. The soil was bottled and stored in a dry, dark place for 20 days before the first extractions. On the assumption there were no phenol losses during evaporation or storage, the expected final concentrations were 2.14, 2.74, 3.37, 3.02 μg/g for phenol, *o*-, *m*- and *p*-cresol, respectively. Because of the long equilibration period and the slurring technique, it was also assumed the contaminants to be uniformly distributed in the sample and that, because the soil still retained residual moisture throughout the storage period, any analyte–matrix interactions would have occurred —over the weathering period— to a similar extent to those in real contaminated soil of similar properties.

The methods were also tested using a natural soil from a cokery plant (Cokery soil). This soil was kindly supplied by Dr. W. Grossmann from the Institut für Umweltschutz Chemie und Biotechnologie at Essen (Germany) This material is heavily contaminated with cyanides, polycyclic aromatic hydrocarbons and phenols. This soil is considered a difficult matrix to analyse because of the high background levels and a carbon content of 18%.

2.6. Analysis

Analyses were carried out on a Hewlett-Packard HP5890 Series II gas chromatograph equipped with a HP/5971 masss-selective detector operated through a HP ChemStation (DOS-series). Experimental parameters used were as follows: column HP-1 (methylsilicone), 30 m length, 0.2 mm I.D., 0.3-μm film; temperature program, 40°C for 1 min heated to 130°C, ramp 30°C/min and held 4 min; automated injection of 1 μl; injector temperature, 270°C; capillary direct interface temperature 300°C; the MS system operated in the selected ion monitoring (SIM) mode using a single step acquisition monitoring ions 94 (phenol), 108 (cresols) and 146 (1,4-dichlorobenzene). The auto-tune feature was used for tuning the MS system and the recommended electron multiplier voltage was used in analysis (typically at 1400 V).

2.7. Precaution and operation considerations

Microwave processes are deceptively simple and as such, extreme care should be exercised when working with flammable solvents. In cases where the matrix contains constituents which couple strongly with microwave radiation, such as charcoal used in this work, the rapid rise in temperature can lead to potentially hazardous situations. Operators should obtain as much information as possible on the composition of the matrix to be extracted.

3. Results and discussion

3.1. Analytical procedure for derivatised and underivatised phenol and methylphenols by GC–MS

Calibration curves for phenols and acetylphenols were run at four concentration levels using appro-

priately diluted standards. Each concentration level was injected in triplicates. Chromatographic peak areas were plotted by linear regression. The correlation coefficients obtained were 0.9999 for the four compounds.

Using the GC parameters outlined herein, the derivatised phenols are satisfactorily resolved. By comparison, underivatised *m*- and *p*-cresol elute together and it is necessary to use special stationary phases (e.g., DIIDP, diisodecylphtalate) for resolving these compounds [22]. To permit direct comparison with underivatised *m*- and *p*-cresol results, the resolved derivatised species are summed in the data presentation. Because the retention times for the free and derivatised phenols are different, it is possible to determine the efficiency of the acetylation and/or extraction process in a single GC run. The efficiency of the acetylation process was found to be above 98% for the four compounds. Fig. 1 compares the chromatograms obtained by SFE and SFE-derivatisation in the case of the cokery soil sample.

The repeatability of the chromatographic procedure was assessed by performing five consecutive injections of standard solutions containing all four analytes. The relative standard deviation for underivatised and derivatised phenols was around 6%. The detection limits were between 0.6–0.8 ng/g for derivatised phenols and between 2.0–2.8 ng/g for underivatized phenols.

3.2. Phenol recoveries in two spiked soils: garden soil and Endesa soil

For this validation we have performed between 3 and 5 extractions using 1-g sample size. Generally, with derivatisation, the recoveries were slightly lowered, but all four methods gave good recoveries for the four compounds in both soils as can be seen in Table 3. The only exception is *o*-cresol: the SFE-derivatisation recoveries were low (between 62–65% recovery). This is in agreement with earlier work in which optimisation of this SFE-derivatisation method was investigated; the recoveries obtained for *o*-cresol were around 60% [24].

3.3. Effect of increasing charcoal content on phenol recoveries

To study the effect of activated charcoal on the extraction efficiency of phenol and cresols, we prepared a series of artificial soils with activated charcoal content between 2%–10% (w/w). Table 4 summarises the results obtained. The recoveries from the soil with 2% in activated charcoal were good with the four methods. When the charcoal content was at 5% and 10%, the recoveries using MAP extraction were still good with the exception of *o*-cresol (Fig. 1b). This compound exhibits lower recoveries when the content in charcoal is over 5% with both methods: recovery is 50% for MAP-extraction–derivatisation and 30% for MAP-extraction. These data suggest that the increased recovery associated with microwave application is not simply a thermal effect. In fact, in MAP-extraction experiments, an acetone–hexane (80:20) mixture is used, this mixture absorbs a significant portion of the microwaves and causes heat increase whereas in the MAP-derivatisation experiments, where hexane is used, almost all of the microwave energy can apply directly into the matrix thus increasing greatly the ability to free the phenols from the soil sample, in particular from the active sites and from the activated carbon particles surface where the phenols are adsorbed the most. It is believed to be for that same reason that the recovery of *o*-cresol, which traditionally has always been extracted with low recovery, was observed to be significantly enhanced, almost twice the recovery obtained by other means. It must be noted that charcoal is a very efficient coupler of microwave energy, actually, temperature increment of almost 2000°C/min has been reported. This means that special care and safety precautions have to be taken when dealing with this types of matrices.

In summary, the data presented herein demonstrate that microwave assisted extraction is a very powerful technique for extracting phenols from soils, even in the presence of very strong adsorptive charcoal in the matrix.

The influence of the charcoal percentage in soil on phenol recoveries were also studied for the two proposed SFE methods. Table 4 summarises also the results obtained. Recoveries obtained with the supercritical extraction method for the underivatized phenols is good at a charcoal content of 2% but decreases to between 28–51% when the charcoal content is 5%. With a 10% charcoal content, even lower recoveries were obtained (between 7–30%). In contrast, the results obtained with the SFE-derivati-

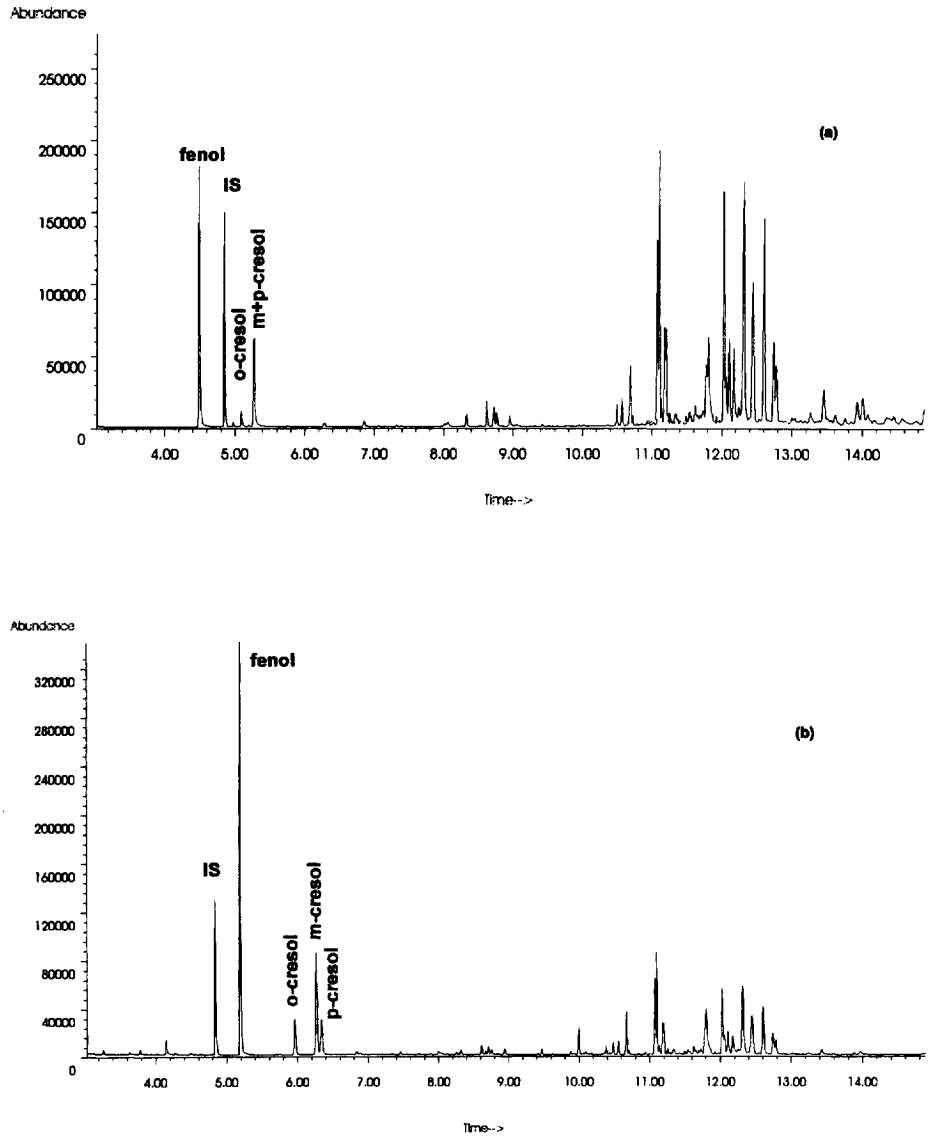

Fig. 1. obtained by SFE (a) and SFE-derivatisation (b) corresponding to the Cokery soil sample.

sation method were very uniform (>77%) and less dependent on the matrix charcoal contents. Again *o*-cresol being the exception, the recoveries were in the 60–70%. The extraction of the underivatized phenols from highly adsorptive matrix also presents a technical challenge to SFE. In our work, extreme experimental conditions were required: a 90°C extraction cell temperature and a density of 0.77 g/ml (resulting from the application of a pressure of 382 bars), represent the maximum that this particular instrument permits.

In conclusion, the two SFE methods are adequate for relatively less adsorptive matrices. However, for difficult matrices the most energetic SFE conditions we have employed for underivatized phenols are not strong enough to break the analytes–matrix interactions. In these cases, an in situ derivatisation process is the solution of this problem and the recoveries

Table 3
Mean recoveries obtained using the four extraction methods in two different soil samples

Soil sample	Compound	Recovery (%)			
		MAP	MAP-derivatisation	SFE	SFE-derivatisation
Garden soil	Phenol	111.5±8	94.7±12	88.0±13	72.0±4
	o-Cresol	90.8±5	80.0±8	90.5±2	62.5±5
	m- + *p*-Cresol	104.9±5	89.8±12	85.9±11	90.2±8
Endesa soil	Phenol	85.0±10	106.0±7	77.5±10	66.0±2
	o-Cresol	77.5±6	85.5±5	80.6±7	65.0±2
	m- + *p*-Cresol	85.3±12	103.2±6	96.0±10	89.5±2

Table 4
Mean recoveries obtained using the four extraction methods in three garden soils with 2, 5 and 10% activated charcoal content

Soil sample	Compound	Recovery (%)			
		MAP	MAP-derivatisation	SFE	SFE-derivatisation
2% Charcoal soil	Phenol	106±15	108±11	97±13	97±5
	o-Cresol	74±8	83±9	83±6	67±7
	m- + *p*-Cresol	103±13	102±10	80±9	84±7
5% Charcoal soil	Phenol	110±17	107±10	52±2	77±4
	o-Cresol	30±3	52±6	32±2	60±4
	m- + *p*-Cresol	85±12	89±8	29±1	88±6
10% Charcoal soil	Phenol	116[a]	102±4	3±1	77±4
	o-Cresol	29[a]	47±2	14±1	60±4
	m- + *p*-Cresol	76[a]	87±2	13±1	88±6

[a] Mean of two extractions.

obtained with this method were very uniform in all the soils tested.

3.4. Validation of the recoveries obtained from a real contaminated matrix

The four methods were also tested with a real cokery soil matrix with a natural 18% carbon content, in addition to a high contamination level of polycyclic aromatic hydrocarbons and cyanides. The μg/g concentration of phenols found are shown in Table 5. Results obtained with the two methods SFE and MAP extraction for the free phenols were similar with the exception of *o*-cresol. For this specific compound, the SFE method recovery proved to be marginal: only 57% percent that of the MAP value. The two extraction–derivatisation methods also showed lower recoveries. No explanation can be offered for the lowered recoveries, but competition/reaction of the background components of the matrix for the reagents (thus leading to incomplete derivatisation) is suspected.

In conclusion, in general the performances of extraction–derivatisation processes are better than

Table 5
Mean recoveries obtained using the four extraction methods for a real Cokery soil

Compound	Recoveries (μg/g)			
	MAP	MAP-derivatisation	SFE	SFE-derivatisation
Phenol	16.8±0.7	10.3±0.3	15.1±0.6	11.0±1.1
o-Cresol	3.7±0.3	1.9±0.1	2.1±0.1	1.6±0.2
m- + *p*-Cresol	10.1±0.4	6.6±0.2	10.3±1.6	6.7±0.3

Table 6
Relative standard deviations (R.S.D.%) obtained using the four extraction methods for two different soil matrices

Compound	Cokery soil				(2% activated charcoal) Garden soil			
	MAP	MAP-derivatisation	SFE	SFE-derivatisation	MAP	MAP-derivatisation	SFE	SFE-derivatisation
Phenol	3.9	2.9	4.2	10.1	14.5	10.4	13.5	4.9
o-Cresol	6.8	3.6	6.3	11.6	11.8	11.6	7.1	9.7
m- + *p*-Cresol	3.8	5.5	15.3	10.8	12.8	9.9	11.4	8.1

extraction alone in that they can provide more specific extraction and higher efficiency (see above), they are less prone to co-extraction of background material because of the milder extraction conditions, and they offer a better chromatography. The case of the Cokery soil points out the importance of further understanding of physical phenomena occurring during extraction processes in order to allow to tackle any matrix, irrespective of its nature.

3.5. Precision of the four methods

Table 6 shows the R.S.D. (%) obtained for a real contaminated soil (Cokery soil) and an artificial spiked aged soil. The R.S.D. obtained for the other soils studied were similar and are not shown for the sake of clarity. The results indicate a precision between 3 and 15% from the overall extraction and analysis procedure. There are no significant differences among all methods; for example, MAP extraction for the Cokery soil showed a precision of 4 to 7%, but in the case of the soil with 2% charcoal, the same method has a precision of 13 to 15%.

3.6. SFE and MAP versus sonication of underivatized phenols

We have extracted some of the matrices utilised in this study with the US EPA sonication method [26], using dichloromethane as a solvent (Table 7). The recoveries obtained were always lower and around 50% of the recoveries achieved with MAP and SFE. The recoveries obtained for the soil with 10% of charcoal were much lower than MAP (only 29%, 7% and 16.8% for phenol, *o*-cresol and *m*- + *p*-cresol) but similar to the recoveries obtained with the SFE method for the underivatized phenols. It has been shown previously that for this matrix the derivatisation step in SFE improves the recovery efficiency drastically. The conclusion was that the results obtained with SFE and MAP were much better than the recoveries obtained with the US-EPA-approved sonication method.

Acknowledgments

Support of the Spanish Inter-Ministerial Commission for Science and Technology under the framework of the project PB92-0372 is gratefully acknowledged. Some supplementary funding from the Environmental Protection Service of the Department of Environment of Canada is also acknowledged. One of the authors (M.P.L.) is indebted to the Spanish Education Ministry for a doctoral grant.

Table 7
Mean recoveries for Endesa soil, Cokery soil and the Garden soil with 10% charcoal using MAP, SFE and Sonic probe extractions

Compound	Endesa soil (% recovery)			Cokery soil (μg/g found)			10% Charcoal-Garden soil (% recovery)		
	MAP	SFE	Sonic	MAP	SFE	Sonic	MAP	SFE	Sonic
Phenol	106	87	56	16.8	15.1	8.3	116.5	31	29.7
o-Cresol	85	81	47	3.7	2.1	1.7	29.1	13.7	7.1
m- + *p*-Cresol	103	96	49	10.1	10.3	5.8	76.8	13.2	16.8

References

[1] Environmental Health Criteria 161: phenol, US Environmental Protection Agency, Cincinnati, USA, 1992.
[2] Environmental Health Criteria 168: cresols, US Environmental Protection Agency, Cincinnati, USA, 1995.
[3] M. Valcarcel and M.D. Luque de Castro, Automatic Methods of Analysis, Elsevier, Amsterdam, 1988.
[4] A. di Corcia, J. Chromatogr., 80 (1973) 69–76.
[5] Y. Hoshika, J. Chromatogr., 144 (1977) 181–187.
[6] S.B. Hawthorne, Anal. Chem., 62 (1990) 633A–642A.
[7] M. Richards and R.M. Campbell, LC·GC Int., 9 (1991) 358–364.
[8] J.R.J. Paré, M.Sigouin and J. Lapointe, US Pat. 5 002 784 (March, 1991).
[9] J.R.J. Paré, US Pat. 5 338 557 (August, 1994); US Pat. 5 377 426 (January, 1995); US Pat. 5 458 557 (October, 1995); US Pat. 1996 (in print).
[10] J.R.J. Paré, J.M.R. Belanger and S.S. Stafford, Trends Anal. Chem., 13 (1994) 176–184.
[11] J.L. Snyder, R. Grob, M.L. McNally and T.S. Oostdyck, Anal. Chem., 64 (1992) 1940–1946.
[12] F.E. Onuska, K.A. Terry and R.J. Wilkinson, J. High Resolut. Chromatogr., 16 (1993) 407–412.
[13] V. Lopez-Ávila, R. Young and W.F. Beckert, Anal. Chem., 66 (1994) 1097–1106.
[14] K. Ganzler, I. Szinai and A. Salgo, J. Chromatogr., 520 (1990) 257–262.
[15] F.E. Onuska and K.A. Terry, Chromatographia, 36 (1993) 191–194.
[16] J.W. Hills, H.H. Hill, Jr. and T. Maeda, Anal. Chem., 63 (1991) 2152–2155.
[17] H. Lee, T.E. Peart and R.L. Hong-You, J. Chromatogr., 636 (1993) 262–270.
[18] M.P. Llompart, R.A. Lorenzo, R. Cela, J. Paré, M. Belanger and K. Li, Abstracts Book of the VI Latin American Congress on Chromatography, Caracas, Venezuela, 1996, pp. 25–F11.
[19] M.P. Llompart, R.A. Lorenzo, R. Cela, J. Paré, M. Belanger and K. Li, J. Chromatogr. A, in press.
[20] J.L. Snyder, R. Grob, M.L. McNally and T.S. Oostdyck, J. Chromatogr. Sci., 31 (1993) 183–191.
[21] E.G. van der Velde, M. Dietvorst, C.P. Swart, M.R. Ramlal and P.R. Kootstra, J. Chromatogr. A, 683 (1994) 167–174.
[22] M.P. Llompart, R.A. Lorenzo and R. Cela, J. Chromatogr. A, 723 (1996) 123–134.
[23] M.P. Llompart, R.A. Lorenzo and R. Cela, J. Chromatogr. Sci., 34 (1996) 43–51.
[24] M.P. Llompart, R.A. Lorenzo and R. Cela, J. Microcol. Sep., 8 (1996) 163–174.
[25] M.P. Llompart, R.A. Lorenzo, R. Cela and J.R.J. Paré, Eighteenth International Symposium on Capillary Chromatography. Volume II, Riva del Garda, Italy, 1996, pp. 912–921.
[26] US EPA (1988) US EPA Contract Laboratory Program Statement of Work for Organic Analysis: Semi-volatile Compounds. Washington, DC, US Environmental Protection Agency, pp. D1/SV45/SV.