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Phenol and methylphenol isomers determination in soils by in-situ microwave-assisted extraction and derivatisation

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Abstract

A simultaneous microwave-assisted extraction–derivatisation procedure was developed and optimised for phenol and methyl phenol isomers from soil samples. Both spiked and real soil samples (carbon content of 18%) were irradiated with microwaves in a closed-vessel system while immersed in hexane that had been previously doped with acetic anhydride and pyridine so as to effect an in situ catalytic acetylation of the target phenolic compounds. Spiked samples were prepared at least 20 days before treatment to simulate natural weathering processes and allow for the formation of analyte–matrix interactions. Optimization of the method was achieved by using a factorial design approach on parameters such as the volume of solvent, the quantity of acetic anhydride and the extraction temperature. Comparison with ultrasonic extraction procedures indicated that microwave-assisted methods gave superior recoveries (ca. two-fold) and greater precision in addition to being characterised by shorter extraction times. The procedure using microwaves yielded samples that could be analyzed directly on a GC–MS system without any preliminary clean-up or concentration steps. The detection limit of this novel method was found to be in the low-ppb range.

Keywords: Microwave-assisted extraction–derivatisation; Derivatization, GC; Phenol; Methylphenols

1. Introduction

In the last few years microwave-assisted processes have become not only interesting but practical alternatives in many fields of chemistry and industrial processes. For years it has been used advantageously for the digestion of environmental and biological samples in inorganic analysis [1]. Later, the applicability of microwaves for the extraction of various types of organic compounds from soil, foods and feeds was investigated [2–4]. Environment Canada has been specially active in this field, developing and patenting a number of applications [5,6] as part of its continuing program on microwave-assisted processes (MAP)[1]. The most widely known ones to date make use of microwave energy to extract soluble products from different matrices using organic solvents. In general the compounds can be extracted more selectively and more quickly

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with similar or better recovery when compared to conventional extraction processes. Also microwave extraction uses less solvent and energy than conventional techniques [4]. The first fundamental applications of MAP that were reported dealt with the extraction of aromas and flavours from plant material, although the technology applies to the extraction of a variety of chemical substances from a wide range of matrices such as soils, plant and animal tissues, as well as a variety of man-made products [4–10].

Recently, a number of microwave-liquid-phase extraction applications have been reported. In the environmental analysis sector, for example, Onuska and Terry extracted organochlorinated pesticides from sediments [11], PCBs from water [12]; Fish and Revesz [13] extracted organochlorinated pesticides from soil; Hasty and Revesz [14] used microwaves to enhance the extraction of petroleum hydrocarbons from soil; Lopez-Avila and co-workers [15–17] reported on the microwave-assisted extraction of various groups of pollutants such as PAHs, PCBs, pesticides, phenolic compounds and base/neutral compounds in soils and sediments; Donard and co-workers [18,19] have reported the microwave-extraction of organotin compounds prior to their derivatisation and analysis. In all these studies, the use of microwaves to assist in the extraction of target analytes proved to be similar or more efficient than conventional batch, Soxhlet and ultrasonic methods. To date, all of the reported extraction data were obtained for target analytes in their native form. However, it is well known that some species can be determined more accurately and more efficiently after a suitable derivatisation step; while others can be more efficiently extracted once derivatised. These derivatisation–extraction techniques have been reported recently for supercritical fluid extraction [20–23]. Given the high efficiency reported for microwave-assisted extraction processes, it appeared fully warranted to further explore the possibility of combining an in situ derivatisation step as a means to further enhance the efficiency of the overall analytical protocols for target analytes that are known to benefit from a derivatisation step prior to determination and quantitation.

In this study, we report on the microwave-assisted extraction–derivatisation of phenol and the three methyl phenols (cresols) from soils in a closed-vessel system. The solvent employed was hexane modified with acetic anhydride (derivatisation agent). A factorial design approach was used to optimise the extraction–derivatisation parameters. The spiked soil used in the optimization procedures was prepared at least 20 days before extraction and kept stored in conditions allowing analyte–matrix interactions. Parameters studied included volume of solvent, quantity of acetic anhydride and extraction temperature. Spiked soils and a real soil with a high carbon content (18%) were treated by this procedure using the optimal conditions obtained from the experimental design. Comparative extractions were performed using ultrasonic extraction. The results indicated significantly higher recoveries when microwaves were used (ca. two-fold) with soils with high organic content and overall better precision, as well as being characterised by shorter combined extraction–derivatisation times (six samples were extracted–derivatised simultaneously in 30 min although the specific parameters were not optimised for the 12-sample capacity of the instrumentation used).

It must be stressed that the findings of this study apply only to the optimization of the combined extraction–derivatisation steps, as they were performed simultaneously without attempting to measure the respective kinetics for the extraction step or the subsequent derivatisation step. It worth noting, however, that all microwave-assisted-process-related extractions reported to date have been shown to occur on a much shorter time scale than that of the combined procedures reported herein.

2. Experimental

2.1. Safety considerations

Microwave-assisted processes are simple and can be readily understood in terms of the operating steps to be performed. However, the application of microwave energy to flammable organic compounds, such as solvents, can become hazardous in inexperienced hands. Given the fact that the chemical and physical principles underlying the technology are deceptively simple, an extraordinary level of safety and attention to detail when planning and performing experiments

must be used by all personnel dealing with microwaves. The authors urge all readers to ensure that they seek proper information from knowledgeable sources and that they do not attempt to implement these techniques unless proper guidance is provided. Only approved equipment and scientifically sound procedures should be used at all times. The simplicity associated with the use of microwaves can enhance the level of hazard and exposure to accidents if procedures are not properly assessed and if due care and proper safety measures are not implemented prior to experimentation [1].

2.2. Microwave-assisted extraction–derivatisation

Microwave-assisted extraction–derivatisation experiments were performed with a MES-1000 microwave extraction system (CEM, Matthercos, NC, USA) equipped with a 12-sample tray and pressure and temperature feedback/controls. A 0.5–5 g aliquot of soil was accurately weighed into a Teflon-lined extraction vessel; 200 μl pyridine, 800 μl acetic anhydride and 9 ml of hexane were added to each sample. The extraction vessels were closed after ensuring that a new rupture membrane was used for each extraction. For the purpose of this study, 1–6 simultaneous extractions were performed at full power in less than half-an-hour at a temperature of 130°C. Once the exposure to microwaves completed, the sample carousel was removed from the microwave cavity and cooled in a water bath. For added safety, the control vessel was returned to the microwave to check that the contents were at room temperature before opening. Solvent loss was checked in randomly selected experiments and was found to be below 1%. Using a glass pipette, 1 ml of the clear supernatant was transferred to the injection vial and the raw extract was analyzed by GC–MS without any preliminary clean up or concentration procedure.

2.3. Ultrasonic-extraction–derivatisation

Ultrasonic-extraction–derivatisation experiments were performed using 0.5–5 g samples of soil and an ultrasonic probe (Braun-Sonic U 2000, 175 W). The soil samples were submitted to ultrasound for 15 min with continuous full power with identical chemical conditions as for the microwave-assisted work, namely 200 μl pyridine, 800 μl acetic anhydride and 9 ml hexane. The solvent/soil suspensions were weighed before and after extraction and the final volume was adjusted to make up for any solvent loss. The extracts were analyzed without any clean up or concentration steps. To test the efficiency of derivatisation under ultrasonic-extraction conditions, a neat solution of the free phenols mixture were submitted to the same experimental conditions and proved to be capable of yields in excess of 98%.

2.4. Reagents and chemicals

The standards used were supplied by Aldrich Chemical (Madison, WI, USA). Acetic anhydride was purchased from BDH (Toronto, Canada); pyridine, methanol and *n*-hexane from Caledon (Belleville, Canada). The phenol stock solutions were prepared by weighing an appropriate amount of the standard and dissolved in 10 ml of hexane. Working solutions were made by appropriate dilution of the stock solutions. All the solutions were stored at 5°C in the dark when not in use. For quantitative gas chromatographic determinations, calibrations were carried out at four concentration levels spanning the range 5–10 000 ng/ml. To derivatise the standard solution, 20 μl pyridine and 50 μl of acetic anhydride were added to an overall volume of 0.94 ml of phenol standard. Solutions were maintained in isothermal conditions at 80°C for 30 min prior to gas chromatographic analysis.

Optimization experiments were carried out using a spiked garden soil sample obtained from the Environmental Technology Centre (Ottawa, Canada), the carbon content of which was three percent (3%). The soil was dried in an oven at 90°C for 48 h, ground and sifted to a particle size below 300 μm. A 300-g aliquot was mixed with 400 ml of methanolic phenol solution. The sample was then allowed to air-dry with occasional stirring at ambient temperature, protected from air draught for 7 days. The soil was bottled and stored in a dry, dark place for 20 days before the first experiments. Assuming that no losses of phenol occurred during drying or storage, the expected final concentrations were taken as 1.41, 1.55, 1.65 and 1.70 μg/g for phenol, *o*-cresol, *m*-cresol and *p*-cresol, respectively. It was also assumed

that the contaminants were 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 an extent similar to those in real contaminated soil of similar properties.

The method was also tested using a real soil from a coke plant. This material is heavily contaminated with cyanides, polycyclic aromatic hydrocarbons, phenol and the three cresols, among others. This soil is considered a difficult matrix to analyze because of high background levels and a carbon contents of 18%.

2.5. Analysis

Analyses were carried out on a Hewlett-Packard HP5890 Series II-HP/5971 MSD operated through a HP ChemStation software (G1034). Experimental parameters used were as follows: column, 30 m HP-1, 0.25 mm I.D., 0.3 μm film; temperature program, 40°C for 1 min heated to 130°C at 30°C/min and held for 4 min; automated injection of 1 μl; injector temperature, 270°C; capillary direct interface temperature 300°C; MS operated in selected ion monitoring (SIM) mode using a single-step acquisition, monitoring ions 94 (phenol) and 108 (cresols); the automatic tuning feature was selected and the electron multiplier was operated at a nominal value of 1400 V.

3. Results and discussion

3.1. Optimization of the overall sample preparation procedure

As noted in Section 2.5 above, calibration curves were run at four concentration levels using appropriately diluted and derivatised standards. Each concentration level was injected in triplicate. Chromatographic peak areas were fitted by linear regression; the results are reported in Table 1.

The repeatability of the chromatographic procedure was assessed by performing five consecutive injections of a derivatised standard solution at two different concentration levels, namely 6 and 1000 ng/l. Evaluation of background signal-to-noise ratio ($S/N=3$) indicated a detection limit below 1 ng/ml, and a quantitation limit ($S/N=10$) in the 2 ng/ml range. These results are also presented in Table 1.

Using the GC parameters outlined above the derivatised phenols are well resolved. By comparison, underivatised *m*- and *p*-cresol co-elute. Because the retention times for the free and derivatised phenols are different (Fig. 1), it is possible to determine the efficiency of the acetylation as well as the extraction processes in a single GC run. The derivatization efficiency was greater than 98% for all four compounds. Benefits of acetylation include four times enhancement in sensitivity, better peak shape (less tailing) and complete resolution of all the target compounds.

3.2. Factorial design. Evaluation of the acetylation process using microwave energy

For assessing the microwave-assisted derivatisation alone, we developed a central 2^3+star, orthogonal composite design, involving 16 runs [24–26]. The variables selected were time, quantity of pyridine and quantity of acetic anhydride. The high and low levels assigned to the variables, as well as the values for the fixed factors are reported in Table 2 along with the final temperature recorded in every experimental run. Table 3 summarises the design

Table 1
Calibration and statistical parameters

	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
Linear range (ng/ml)	5.5–8280	6.0–9000	6.4–9630	6.6–9900
Correlation coefficient	0.9999	0.9999	0.9999	0.9999
Detection limit (ng/ml)	0.80	0.65	0.79	0.79
Quantification limit (ng/ml)	2.66	2.15	2.63	2.63
R.S.D. (6 ng/ml)	3.7	6.7	4.7	7.1
R.S.D.(1000 ng/ml)	7.4	6.9	6.1	6.6

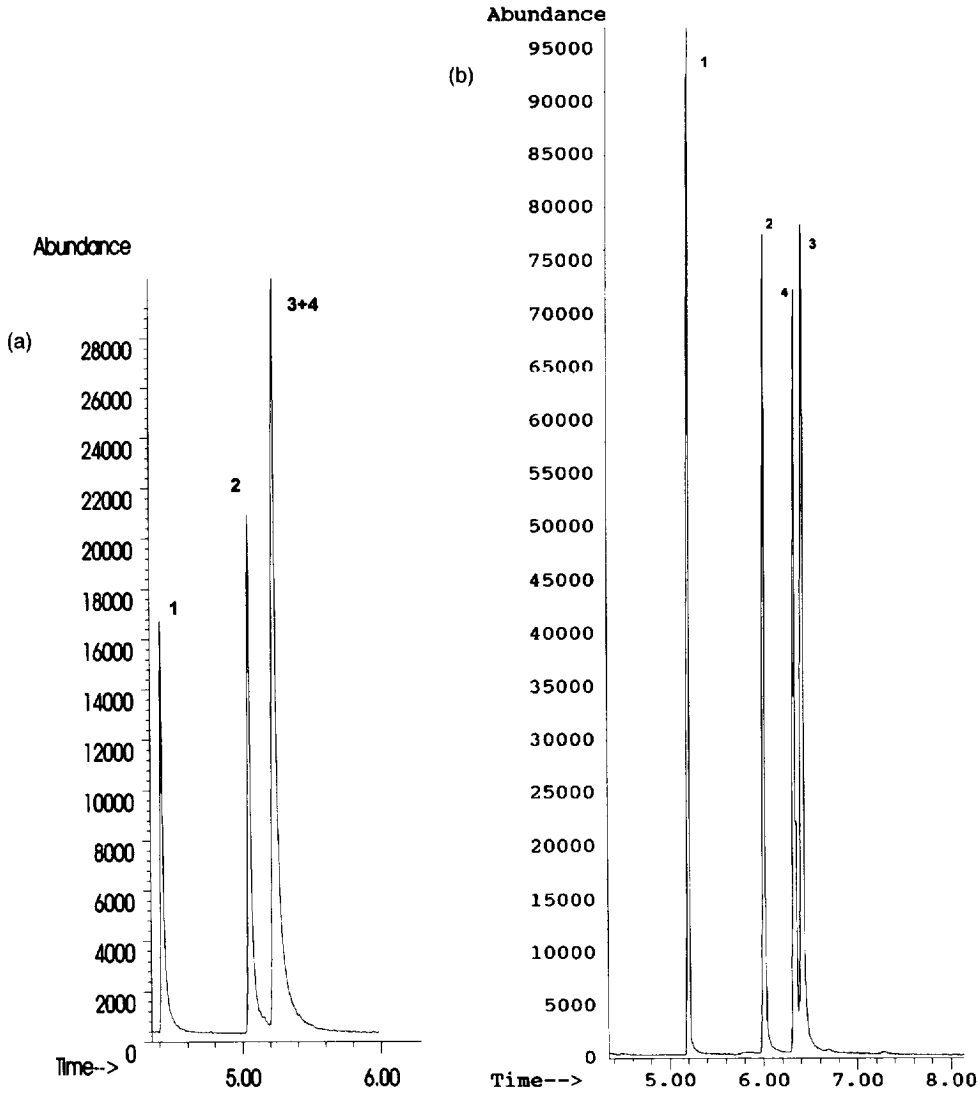

Fig. 1. Chromatograms of (a) underivatized and (b) derivatized phenols. (1) Phenol; (2) *o*-cresol; (3) *m*-cresol and (4) *p*-cresol.

Table 2
Microwave-assisted process parameters employed and optimum values

	First factorial design	Homogeneity study	Second factorial design	Optimum values
Temperature (°C)	–	100	60–140	130
Quantity of acetic anhydride (μl)	100–500	500	200–1000	800
Volume of solvent (ml)	10	10	10–30	10
Quantity of pyridine (μl)	50–200	200	200	200
Time (min)	2–10	20	20	5
Sample size (g)	–	2	5	0.5–5

Table 3
Design matrix and response in the first (central composite) factorial design

Run	Time	Acetic anhydride	Pyridine	Percentage of phenols unreacted		
				Phenol	*o*-Cresol	*m*+*p*-Cresol
1	0	0	0	8.6	27.5	10.3
2	+	+	+	<1.0	1.1	<1.0
3	0	+[a]	0	<1.0	3.9	<1.0
4	+[a]	0	0	3.3	17.3	4.9
5	0	0	−[a]	16.3	35.0	19.1
6	0	0	+[a]	4.9	21.2	8.1
7	−[a]	0	0	14.2	36.3	20.2
8	−	−	+	42.8	53.8	40.6
9	−	−	−	55.6	63.2	48.5
10	+	−	−	38.1	48.8	29.5
11	+	−	+	32.6	50.5	34.2
12	−	+	+	<1.0	8.0	1.9
13	0	−[a]	0	52.5	52.5	43.9
14	+	+	−	<1.0	5.9	<1.0
15	−	+	−	2.2	13.3	4.6
16	0	0	0	6.0	17.3	4.5

[a] = 1.215.

matrix and the results showing the percent of unreacted phenols remaining in the system after each experimental run. The results obtained for underivatised *m*- and *p*-cresols are reported together because, as stated above, they were not resolved under the operating conditions used herein.

The analysis of the results given in Table 3 produced the main effects Pareto chart [26] shown in Fig. 2, which is the result of combining the individual Pareto chart for each species. Although not directly supported by the statistical package used [26], by combining the Pareto charts, a direct

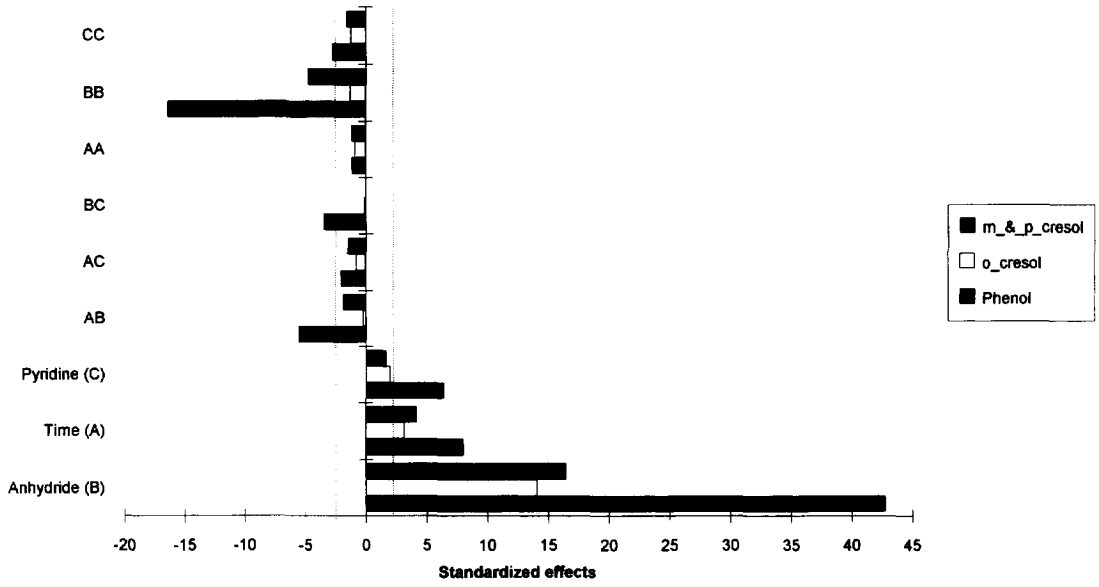

Fig. 2. Combined Pareto chart for the standardized main effects in the first (central composite) factorial design, including two-factor interactions. Dotted vertical lines indicate the statistical significance bound for the effects.

comparison of the results for the four compounds can be made. It can be concluded that time and quantity of derivatising agent were statistically significant for the four compounds. The reaction yield was directly proportional to those two variables (Fig. 3). The quantity of pyridine was not significant, however in the case of phenol Pareto-bar (Fig. 2) appears over the statistical boundary. This was expected since pyridine acts as a catalyst in these reactions.

In conclusion, the derivatisation process for readily available free phenols in solution is complete to near 99% using microwave energy within 10 min (see run No. 2 in Table 3).

3.3. Evaluation of the homogeneity of the laboratory-spiked soil sample

For testing the homogeneity of the spiked sample which was used in optimising the extraction–derivatisation process, a set of six 2-g samples was submitted to conditions reported in the third column of Table 2. The average recoveries obtained were 72.3, 43.9, 63.1 and 53.3% for phenol, *o*-cresol, *m*-cresol and *p*-cresol, respectively. The variability (C.V. between 3.4–8.5) was similar to that obtained from injection of calibration standards alone (Table 1).

In conclusion, the material used was for all practical purposes homogeneous in terms of its contents in the target analytes.

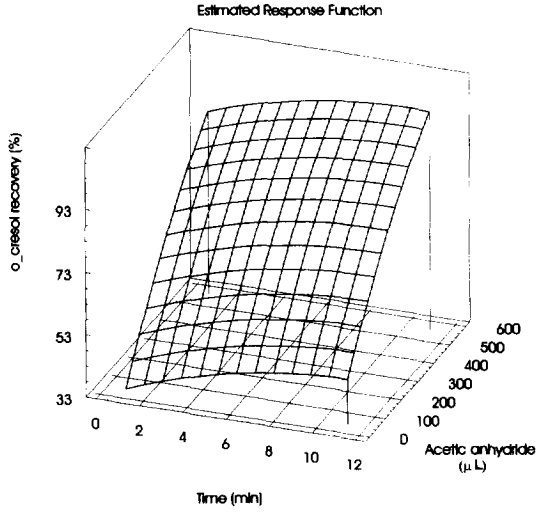

Fig. 3. Response surface estimated for the design in Table 3, obtained by plotting the two statistically significant main factors.

3.4. Optimization of the extraction–derivatisation process. Evaluation of the response surfaces

The variables considered in the extraction–derivatisation optimization procedure were temperature, volume of solvent and quantity of acetic anhydride (derivatisation agent). A three-level central 2^3+star, orthogonal composite design involving 16 runs was chosen [24–26]. This model allows the direct evaluation of the variables considered, as well as the interaction terms. The low and high levels assigned to the variables regarding the value assigned to the fixed factors are listed in Table 2. Table 4 shows the design matrix for this experiment and the recoveries obtained in each experimental run.

An analysis of the results given in Table 4 produced the Pareto chart shown in Fig. 4, which is the result of combining the individual Pareto chart for each species. As can be seen from Table 4, temperature and quantity of acetic anhydride were statistically significant in all cases, with the exception of *m*-cresol. Also, the volume is significant for *o*- and *p*-cresol. The interaction terms between variables were not significant with the exception of the quadratic term for the quantity of acetic anhydride.

Fig. 5a shows the response surface function developed by the model considering temperature and quantity of acetic anhydride in the case of *m*-cresol (response surfaces modelled for the other studied compounds led to identical conclusions). As can be seen, the overall extraction–derivatisation efficiency was directly proportional to the temperature. The acetic anhydride curves present fairly broad maxima, showing optimum efficiency at about 800 µl. This maximum is attributed to the quadratic term (CC) which appears in the Pareto chart (Fig. 4). Fig. 5b shows the response surface obtained for solvent volume and acetic anhydride in the case of *p*-cresol. The extraction–derivatisation efficiency increases for small volumes of solvent – note that in Fig. 4 this factor is affected by a negative sign; however, the influence of this variable is not very important when working with high anhydride levels. This correlation can be explained by the fact that, when using high

Table 4
Design matrix and response in the second (central composite) factorial design

Run	Temperature	Solvent volume	Acetic anhydride	Percentage recovery			
				Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
1	0	0	0	87.9	40.6	70.2	50.7
2	+	+	+	100.0	49.8	63.7	58.5
3	–	+	–	40.5	16.4	39.2	29.6
4	+	–	–	73.2	34.1	69.9	52.8
5	+[a]	0	0	102.2	51.6	79.7	63.2
6	+	–	+	95.6	50.0	75.4	61.4
7	–[a]	0	0	58.8	35.7	55.4	47.6
8	–	+	+	54.7	33.4	55.9	40.2
9	+	+	–	72.1	31.3	54.0	46.0
10	0	+[a]	0	83.0	37.3	70.1	48.0
11	–	–	+	67.1	37.3	58.5	46.4
12	0	–[a]	0	81.5	47.9	70.8	55.5
13	0	0	–[a]	46.5	17.0	37.2	30.4
14	–	–	–	70.1	37.8	69.9	49.3
15	0	0	+[a]	81.7	44.9	69.9	53.3
16	0	0	0	72.6	41.0	69.5	51.5

[a] = 1.215.

anhydride levels, the concentration in solution is high, despite the relatively large volume of 30 ml – the maximum considered. When the quantity of acetic anhydride is reduced, the ratio between these two variables is also reduced for such a volume (30 ml) and, consequently, leads to a reduced extraction–derivatisation efficiency. This, however, is not likely to be the only factor involved since the analysis of the results (Pareto chart, Fig. 4), shows that the interaction term (BC) was not significant.

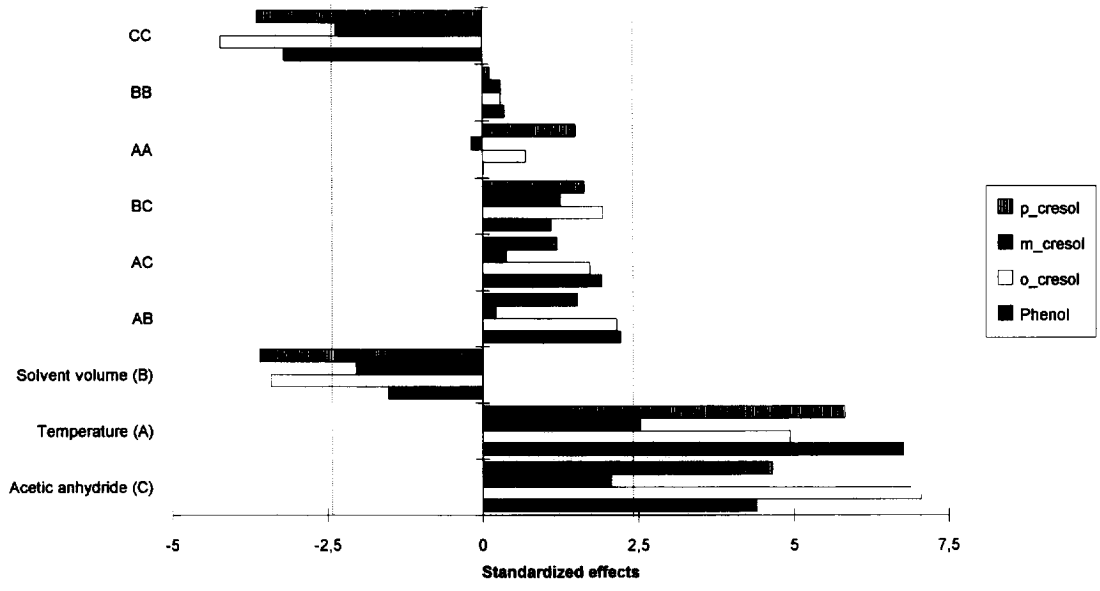

Fig. 4. Combined Pareto chart for the standardized main effects in the second factorial design. Dotted vertical lines indicate the statistical significance bound for the effects.

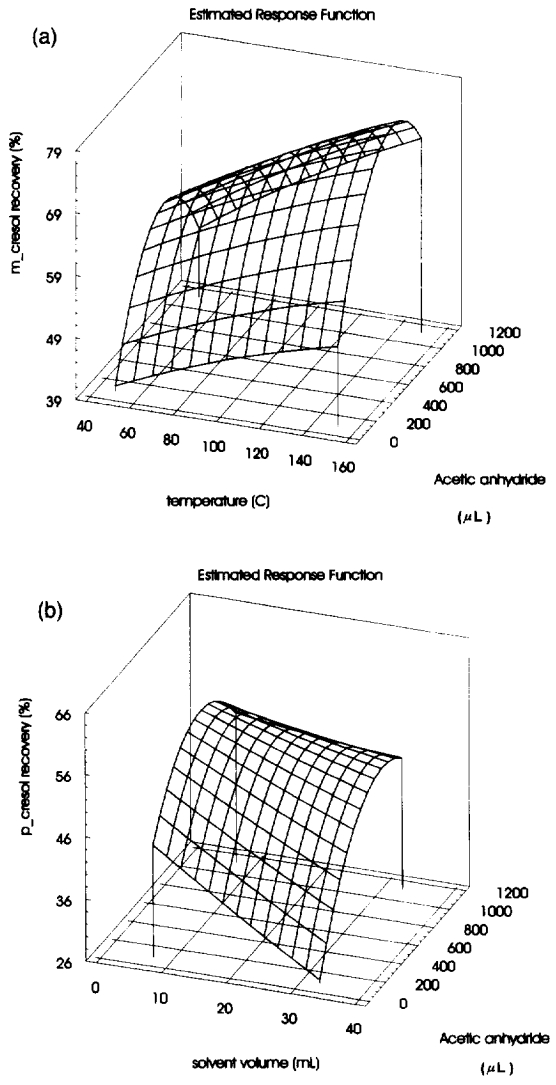

Fig. 5. Response surfaces estimated for the design in Table 4, obtained by plotting: (a) temperature vs. derivatizing agent and (b) solvent volume vs. derivatizing agent.

As a result of these findings, subsequent work was performed under following conditions: 10 ml solvent, 800 μl acetic anhydride and 130°C (Table 2 under optimum values heading). The selection of this temperature was based upon the consideration of practical attainment of maximum temperature when working with small amounts of soils, as well as the soil matrix. Depending on the matrix and the quantity of soil, the maximal temperature that can be reached by the system using microwave energy is different. Use of slightly lower temperature than maximum also promotes a longer service life of the Teflon vessels and minimises concentration or break down of background material that could lead to subsequent interference during the analytical procedures.

3.5. Simultaneous extractions, sample size and extraction time

Using the same soil and the optimal conditions developed above (Table 2, last column), single and multiple (6 samples) extraction–derivatisation experiments were performed. The results obtained were identical within the experimental error. Another set of experiments were also performed: one working with 0.5 g sample size (20 min of extraction–derivatisation time) and a second one with 5-g sample size portions and 5-min extraction–derivatisation period, once the temperature had reached 130°C. The recovery results are again identical for all these extractions. Fig. 6 summarises the results obtained.

In summary, single or multiple extraction can be performed successfully with various sample sizes ranging at least between 0.5 and 5 g using a microwave exposure time as short as 5 min after reaching 130°C. Total sample preparation time is less than half-an-hour.

3.6. Performance evaluation of the proposed method

3.6.1. Ultrasonic extraction

For comparison purposes, six 5-g extraction–derivatisation experiments were carried out with the same soil using an ultrasonic probe. The results are plotted in Fig. 6. Ultrasonic extraction recoveries were by 25% lower than MAP-extraction recoveries for all species.

3.6.2. Recoveries at two different levels

The method was also tested at two different concentration levels, i.e. 40 and 400 ng/g, using freshly spiked 5-g soil samples. The average recoveries and R.S.D. values are shown in Table 5. In both cases the recovery of phenols is complete and the R.S.D. is good for the high level, and still acceptable for the low level.

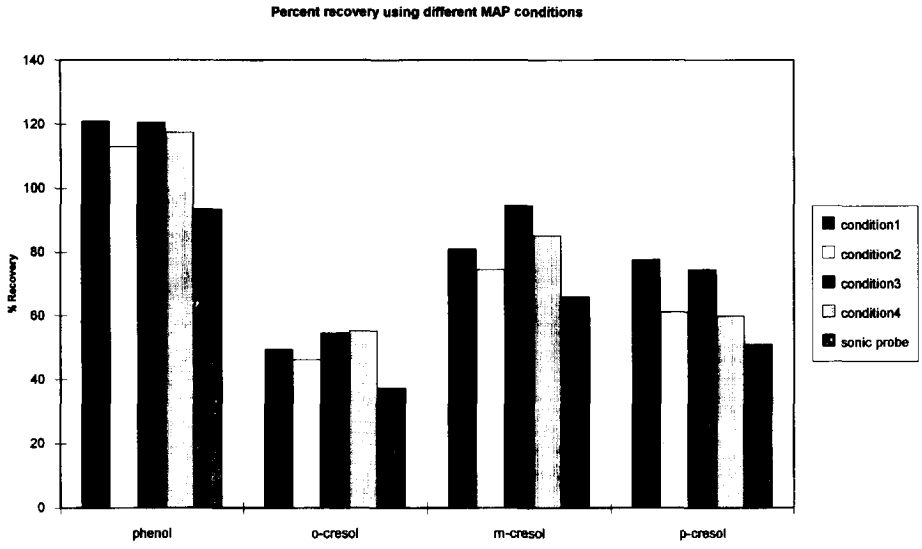

Fig. 6. Percent recovery for the studied species using different MAP conditions and sonic probe. (Condition 1) Single extraction, time 20 min, sample size 5 g; (2) multiple extraction, time 20 min, sample size 5 g; (3) multiple extraction, time 20 min, sample size 0.5 g; and (4) multiple extraction, time 5 min, sample size 5 g.

3.7. Application of the proposed method

Finally, we treated a real soil sample from a coke plant, highly contaminated with a number of pollutants including the four compounds studied in this work. This soil is considered to be a difficult matrix due to its high carbon content (18%). In this type of matrix, the phenols are strongly adsorbed and extraction by conventional techniques has yielded poor recoveries at best. Samples of this soil were also subjected to the method developed herein and to the ultrasonic probe method described herein for comparison purposes. The results of these experiments are summarized in Fig. 7. Ultrasonic results were considerably lower than microwave-assisted results (approximately by a factor of two). Fig. 8 shows a chromatogram of the coke plant soil sample after extraction–derivatisation by the proposed method.

In conclusion, even though the recoveries from easy and moderately-difficult soil matrices are similar using both techniques (ultrasonic probe and microwave-assisted procedure), the use of microwave energy in the extraction–derivatisation of phenols in difficult matrices offers significantly higher recoveries in addition to a much shorter sample preparation time.

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Table 5
Percent recovery in freshly spiked soil at two different concentration levels

	400 ng/g		40 ng/g	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Phenol	98.3	4.0	90.5	12.7
o-Cresol	105.5	7.3	102.9	16.8
m-Cresol	112.1	10.2	103.2	17.2
p-Cresol	106.7	10.6	110.7	21.4

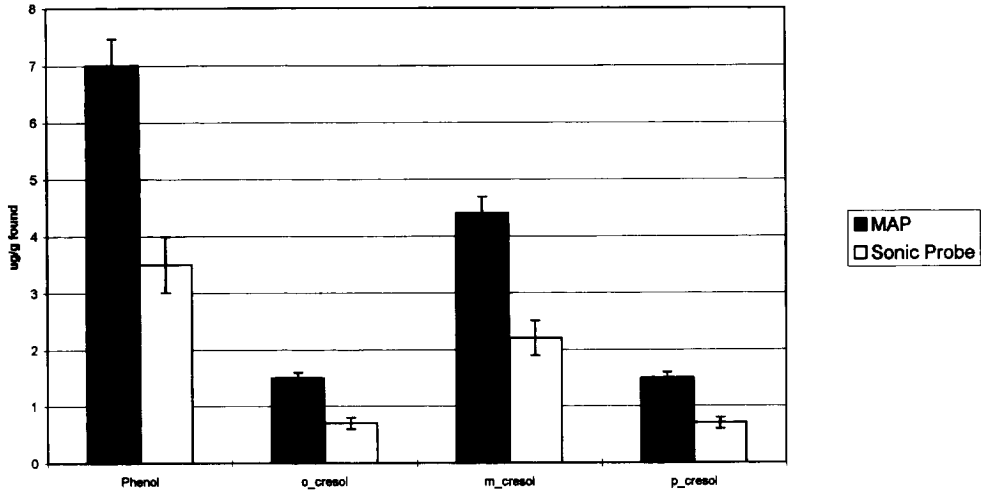

Fig. 7. Comparative results (mean values and standard deviations) in the extraction–derivatisation of a heavily polluted real coke plant soil using the microwave-assisted process and sonic probe.

ence and Technology (Project PB92-0372), the Department of the Environment of Canada (Environmental Protection Service) and to the Dr. W. GroBmann (Institut für Umweltschutz Chemie und Biotechnologie) at Essen who kindly supplied the coke plant soil sample. One of us (MPL) is indebted to the Spanish Education Ministry for a doctoral grant and to the Department of the Environment of

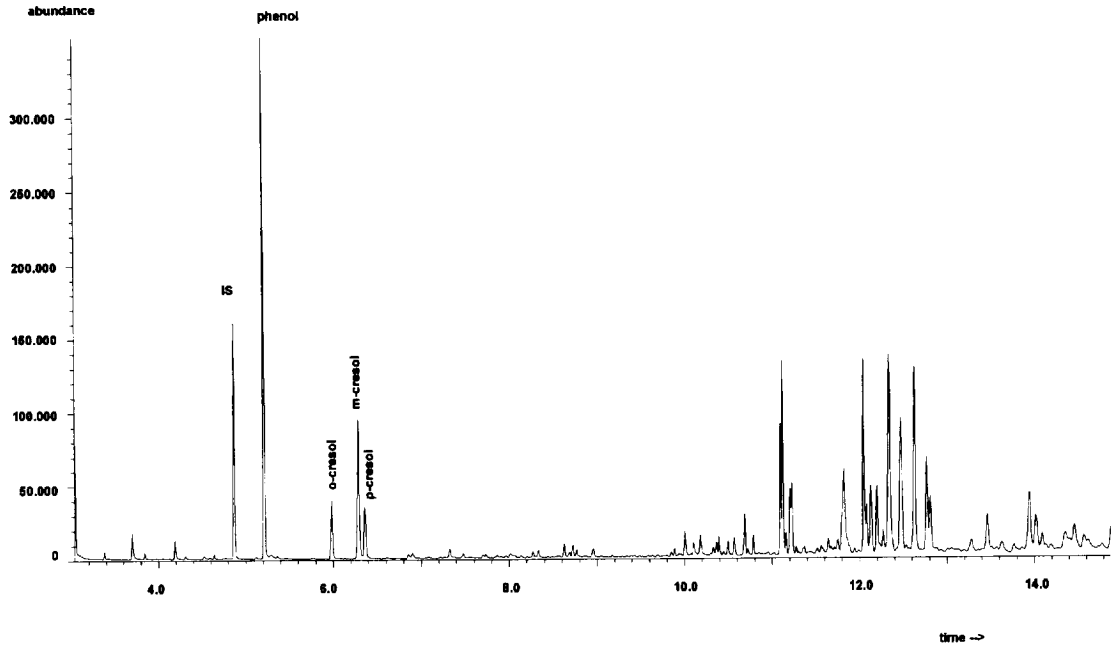

Fig. 8. Chromatogram of a derivatised–extracted coke plant soil sample.

Canada for its hospitality during the course of some of this work.

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