



# Accelerated solvent extraction (ASE) of environmental organic compounds in soils using a modified supercritical fluid extractor

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## Abstract

Accelerated solvent extraction (ASE) has been applied to the quantitative extraction of a selected list of semi-volatiles, which include polycyclic aromatic hydrocarbons (PAHs), phenols, polychlorinated biphenyls (PCBs) and total petroleum hydrocarbons. Two conventional supercritical fluid extraction (SFE) systems, the Suprex Prep Master and SFE/50 systems have been modified to function as ASE systems. Using solvent instead of supercritical fluid, extraction in an enclosed system proceeded under high pressure and temperature. Parameters such as extraction temperature and effect of modifiers were investigated. Although limited by a 150 °C maximum oven temperature, effective extraction could be carried out in less than 25 min for all the compounds studied. The technique was applied to a variety of real matrices contaminated with hydrocarbons, PAHs and phenols. Validations of the technique were performed using standard reference materials. Recoveries for these matrices were good (>75%) and precision (R.S.D.) was generally less than 10%. Primarily a rapid field extraction technique, comparison with other rapid extraction such as sonication and microwave assisted extraction (MAP<sup>TM</sup>) were made. Recoveries were found to be comparable to MAP<sup>TM</sup> and superior to sonication. On the present ASE system, only sequential extraction can be carried out but given the rapid nature of the process, about 15 samples can be carried out in a working day.

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## 1. Introduction

The desire to reduce the use of hazardous organic solvents in analytical extraction has contributed in the last few years to the development of new technologies using less sol-

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vent than classical extraction procedures. Among the new techniques, supercritical fluid extraction (SFE) and microwave assisted extraction (MAP<sup>TM</sup>) have achieved great popularity, evident from the number of applications in environmental analysis. SFE uses carbon dioxide as the principle extraction fluid, thus reducing the usage of hazardous solvent [1]. Extraction utilising microwave energy is a sample extraction technique patented by Environment Canada under the name MAP<sup>TM</sup> [2–4]. This novel technique can also reduce solvent usage and shorten extraction times [5,6].

A recent advance in sample preparation for trace environmental analysis is the accelerated solvent extraction (ASE). This technique uses conventional solvents at elevated pressures and temperatures to extract solid samples quickly [7,8]. The process takes advantage of the increase analyte solubility at temperatures well above the boiling points of common solvents. In addition the kinetic processes for analytes to desorb from the matrix are accelerated.

Currently a commercial unit is available in which automated extractions can be carried out on 24 samples sequentially [9,10]. This technique offers some significant advantages over SFE and MAP<sup>TM</sup>. In the case of extracting polar compounds by SFE, addition of a polar modifier to the non-polar supercritical CO<sub>2</sub> is often necessary. Still very high temperatures and pressures are necessary to achieve quantitative extraction [11], which increases instrument wear and prolongs extraction time. Another disadvantage of SFE is that method development is usually complex and time consuming, due to the large number of variables in instrument parameters and solvent optimisation [12].

MAP<sup>TM</sup> extractions can be performed under closed- or open-vessel conditions. In this form of extraction, the solid sample is heated rapidly in a polar solvent by MW energy. Instrumentation is relatively simple and method development time is greatly reduced. It is, however, subjected to potential interferences from the presence of microwave energy absorbing materials in the sample matrix such as ferrous materials and charcoal, these can cause localised ‘hot spots’ and can be a safety issue. Presence of moisture can also lead to different heating profiles for different sample types. At the end of the extraction, extraction vessels must be cooled to room temperature before they can be opened, thus increasing the overall extraction time. In the early versions of commercial extraction equipment, post-extraction sample workup requires filtration to separate the raw extract from the solid material.

In this work, we studied the feasibility of performing ASE using an SFE instrument as well as the ability of ASE to extract different groups of semi-volatiles (polycyclic aromatic hydrocarbons (PAHs), hydrocarbons and phenols) from soil samples. For this study, two supercritical fluid extraction systems, the Suprex Prep Master and SFE/50 systems, were adapted to operate as ASE systems. Different parameters affecting the extraction efficiency were investigated. Extensive comparison of this technique with sonication and with MAP<sup>TM</sup> was made. Four real contaminated samples were extracted to establish the validity of the proposed method.

## 2. Experimental

### 2.1. Reagents and materials

Analytical reference standard solution (SRM 1491) of the target PAHs was obtained from NIST (Gaithersburg, MD). Working solutions were prepared in hexane. A surrogate

mixture of four deuterated PAH compounds was purchased from Supelco (Mississauga, Ont.).

For hydrocarbon fuel analysis, standards were made by diluting 1  $\mu$ l of the fuel in 1 ml of hexane:acetone.

For polychlorinated biphenyls (PCBs) analysis, analytical reference standard solution of Aroclor 1260 was obtained from Ultrascience (Don Mills, Ont., Canada).

Phenol standards were supplied by Aldrich Chemie (Steinheim, Germany). Standard stock solutions were prepared by weighing an appropriate amount of each standard and diluting to 10 ml with hexane. Working solutions were made by appropriate dilution of the stock solutions.

All solvents were of distilled-in-glass grade and purchased from Caledon (Belleville, Canada).

Four real contaminated matrices were used in this study. The SRS103-100 certified reference material is a soil contaminated with PAHs and was purchased from Fisher Scientific (Fair Lawn, NJ). The SRM 1649 certified reference material is an urban dust certified for five PAHs and with provisional PAH values for another four PAHs. This material was purchased from NIST (Gaithersburg, MD). A naturally diesel contaminated soil is from a sour gas process plant in Alberta and the last soil is from a coke plant in Spain. The cokery soil was obtained as a result of an inter-laboratory comparison exercise sponsored by the Community Bureau of Reference (BCR) of the Commission of the European Community aiming at the certification of a reference soil material for phenol and cresols. This material is heavily contaminated with cyanides, PAHs and phenols among others. Phenol, *o*-, *m*- and *p*-cresol make up more than 80% of the total phenols. This soil is considered a difficult matrix to analyse because of the high level of contamination and a strongly adsorptive matrix of almost 20% (w/w) carbon.

## 2.2. Instrumentation

The Prep Master is an integrated SFE extraction system which pressurises carbon dioxide by a dual piston pump. Our system was not equipped with the collection module and temperature controlled variable restrictor, which led to frequent ice blockages of the capillary restrictor (from the cooling effect of supercritical fluid depressurisation) and hence is not suited for routine application. In this work, the solid sample was loaded into the thimble, which was then filled with an appropriate solvent. The thimble was then closed and placed inside a heated oven. Typically, extraction consisted of 10–15 min equilibration during which the thimble was pressurised to 100 atm at 100 °C. The system then proceeded to the dynamic extraction phase during which the contents of the thimble were swept out through a 50 mm capillary into a vial with a loosely-fitted septum and cap. The sole function of the SF carbon dioxide was to flush out the solvent in the thimble. Because SF carbon dioxide depressurised into a gas, the extraction used only a small amount of solvent used to fill the thimble, resulted in a minimal extract volume which often requires no further concentration and can be analysed directly, thus providing a potential benefit of rapid sample turn around.

Preliminary work with this system suffered from ice blockages in the restrictor, resulting in erratic solvent recovery. Switching to a larger diameter restrictor (75 or 100  $\mu$ m) reduced

this problem but created a new one. Since the system relied on a restrictor to maintain the pressure during the dynamic (collection) phase, a larger diameter capillary did not generate enough back pressure to maintain the high pressure condition. This resulted in low recovery of the solvent initially added to the thimble. On the average only 70–75% of the initial volume was collected. While adequate for qualitative identification work, it was not reproducible enough for quantitative work.

The second system investigated was the Suprex SFE/50 system, which was a research-grade modular SFE system consisting of a syringe pump with a capacity of 240 ml, a system controller and an extraction oven and a heated valve compartment with a four-way selector valve allowing the SF carbon dioxide to be collected in different fractions. For this work, the system was modified with the installation of a manual static/dynamic valve downstream of the thimble, bypassing the four-port selector valve. A cylinder of nitrogen was connected to a three-way purge valve upstream of the thimble normally used to vent pressure of the thimble. This was used to flush out the solvent from the thimble after each extraction. A 0.25 mm i.d. stainless steel capillary was used to direct the solvent from the static valve to an open collection vessel. The syringe pump was simply filled by dipping the stainless steel line normally connected to a SFE grade carbon dioxide into a solvent bottle of hexane and using the 'refill' function on the control module. Throughout this study, the pump seals, made of Teflon/graphite composite material, did not suffer any deterioration from exposure to the solvent.

Typically, the solid was weighed into a 5 ml stainless steel thimble which consisted of a Type C extraction vessel (Suprex), capped with a stainless steel nut and a frit and seal assembly. The syringe pump then delivered the solvent to the thimble and pressurised the system to 100–150 atm. Simultaneously, the oven was heated up to 150 °C. After reaching the experimental conditions (5–10 min), the sample was kept in this pressurized fluid environment for 15 min. The pump was then stopped and the system depressurised by opening the static valve, forcing the raw extract out into a calibrated test tube. When the flow ceased, the purge valve was opened to a 100 psi nitrogen source to flush out the residual solvent from the thimble for about 1 min. The system was returned briefly to a pressurised state for the pump to deliver a few ml of fresh solvent to the thimble to rinse out the system. This procedure was repeated 2–3 times and resulted in a final volume of 10–15 ml.

MAP<sup>TM</sup> experiments were performed in a 950-W MES-1000 microwave sample preparation system using Teflon-lined extraction vessels (CEM Corp., Mathews, NC).

Ultrasonic extractions were carried out in an ultrasonic bath (Branson Ultrasonics Corp., Danbury, CT). Vials of 22 ml equipped with Teflon-lined septa and screw caps were used.

### 2.3. Analysis

PAH, PCB and phenol analysis were carried out on a Hewlett-Packard HP5890 Series II-HP5971 MSD operated through a HP data station with ChemStation software G1034. A 30 m HP-1 capillary column (0.2 mm i.d., 0.3 mm film) was used. Experimental parameters were: injector temperature 270 °C, capillary interface temperature 300 °C; automated injection of 1 µl; MSD operated in selected ion monitoring (SIM) mode. Tuning was performed by auto-tune and the electron multiplier was at a nominal value of 1400 V. The oven temperature program for PAH analysis was: 40 °C for 1 min heated to 170 °C at 30 °C/min; heated

to 240 °C at 4 °C/min; and finally heated to a final temperature of 300 °C at 12 °C/min, and held at this temperature for 10 min. The oven temperature program for PCB analysis was: 120 °C for 1 min heated to a final temperature of 310 °C at 10 °C/min, and held at this temperature for 5 min. The oven temperature program for phenol analysis was: 40 °C for 1 min heated to 130 °C at 30 °C/min and held for 4 min. Prior to injection, an internal standard of d14-Terphenyl was added to give a final concentration of 1 µg/ml. Quantitation was based on internal standard method.

For total hydrocarbon analysis a 5890 GC equipped with a flame ionisation detector (FID) was used. A DB-5 column (30 M, 0.25 mm i.d. with 0.25 mm film) was used. Oven temperature was 50 °C for 1 min and heated to 310 °C at the rate of 15 °C/min. One milliliter was injected splitless via an auto-sampler. Injector and detector temperature were 280 and 310 °C, respectively. The GC column flow was nominally 1 ml/min. Quantitation was carried out using manual integration of the unresolved hydrocarbon envelop between carbon number 12 and 22. The area total was used to compute the amount of fuel present in the sample by comparing to an external standard.

#### 2.4. ASE procedure

A 0.1–2 g aliquot of soil was weighed in an extraction thimble; for PAH analysis a surrogate mixture was added just prior to extraction. For most of the extractions, a polar solvent as a modifier was added just before extraction. The end caps of the cell were hand tightened. The extraction program consisted of 15 min static extraction at 100 atm and 50–150 °C. The solvent used was hexane. After extraction, the raw extract was collected as noted above. The extract was analysed directly or after concentration by nitrogen blow-down.

#### 2.5. Closed-vessel MAP<sup>TM</sup> extraction procedure

A 0.1–2 g aliquot of soil was weighed into the Teflon extraction vessel and 10 ml of hexane:acetone (1:1) were added. For PAH analysis, an aliquot of surrogate mixture was added to the sample just prior to the addition of the solvent. The extraction vessel was closed, after ensuring that a new rupture membrane was used for each extraction. Generally 3–6 samples were extracted simultaneously at 115 °C for 20 min at 100% power. After extraction, the vessels were allowed to cool in a water bath before opening. The supernatant was filtered through a 45 µm nylon disk and made to a known volume. In the case of low analyte concentration, concentration by nitrogen blow-down was necessary before analysis.

#### 2.6. Ultrasonic extraction

A 0.1–2 g aliquot of soil was weighed in a 22 ml glass vial. Samples were extracted with 5 ml aliquots of hexane:acetone (1:1) for 20 min and the process was repeated two more times with fresh solvent (3 × 5 ml total). For PAH analysis a surrogate mixture was added to the sample just prior to extraction. The combined extract was filtered and analysed without any clean-up. In some cases concentration by rotary evaporation and nitrogen blow-down was necessary.

### 3. Results

#### 3.1. Collection procedure

Preliminary work was performed using artificially spiked samples. The temperature and pressure were 100 °C and 100 atm. The soil matrix consisted of a garden soil from an urban location, prepared by air-drying, crushing and screening to 200 µm particle size. Hydrocarbon fuel mixtures (diesel and jet) as well as Aroclor 1260 were used to spike this soil at 2 µg/g. Initially collection was made without any rinsings of the thimble. This was found to give highly variable recovery figures because of the residual solvent left in the thimble after depressurisation (up to 25%). The optimized collection procedure required the thimble to be rinsed 2–3 times with several milliliters of fresh solvent and purged each time using high pressure nitrogen. With this procedure, quantitative recoveries of the spiked analytes were obtained. The mean of the triplicate fuel spike recovery was 82.4% and for Aroclor recovery was 98.0%. Residual amount of spike found in a second extraction of the same sample was generally less than 5%.

#### 3.2. Effect of modifier addition

In all our studies the extraction solvent used was hexane. The effect of adding acetone as a polar modifier was investigated. The modifier can be added to the extraction cell or to the solvent container refilling the syringe pump. The role of a polar modifier in ASE is similar to that in SFE, which functions to improve the solubility of polar analytes, to help in weakening of the analyte–matrix interactions and to compete with the analytes for the active sites on the matrix surface. For these studies, the cokery soil contaminated with PAHs and phenols was used. The results of PAH extraction are illustrated in Fig. 1. For the five-ring compounds, the recoveries without the addition of a modifier were around 70% of the ones using modifier. For the six-ring PAHs the benefit of using modifier was more pronounced: without modifier recoveries were only 50% of those using modifier.

Due to the polar nature of phenolic compounds the addition of a polar co-solvent was essential for quantitative extraction. As can be seen in Fig. 2, the recoveries obtained without the addition of modifier were only 15–30% of the recoveries using modifier. For these compounds, we also investigated using methanol instead of acetone as well as different amounts of acetone (0.2 and 2.5 ml). Recoveries were essentially identical in all cases.

#### 3.3. Effect of extraction temperature

The temperature study was confined to the 150 °C maximum operating temperature of the oven. For all soil matrices studied in this work, we found it was high enough to effect quantitative extractions of all target analytes.

The effect of the temperature was studied using standard reference material (Urban Dust SRM 1649) contaminated with PAHs. The material was extracted at temperatures of 50, 100 and 150 °C and the results are shown in Table 1. For this matrix, even at 50 °C, ASE

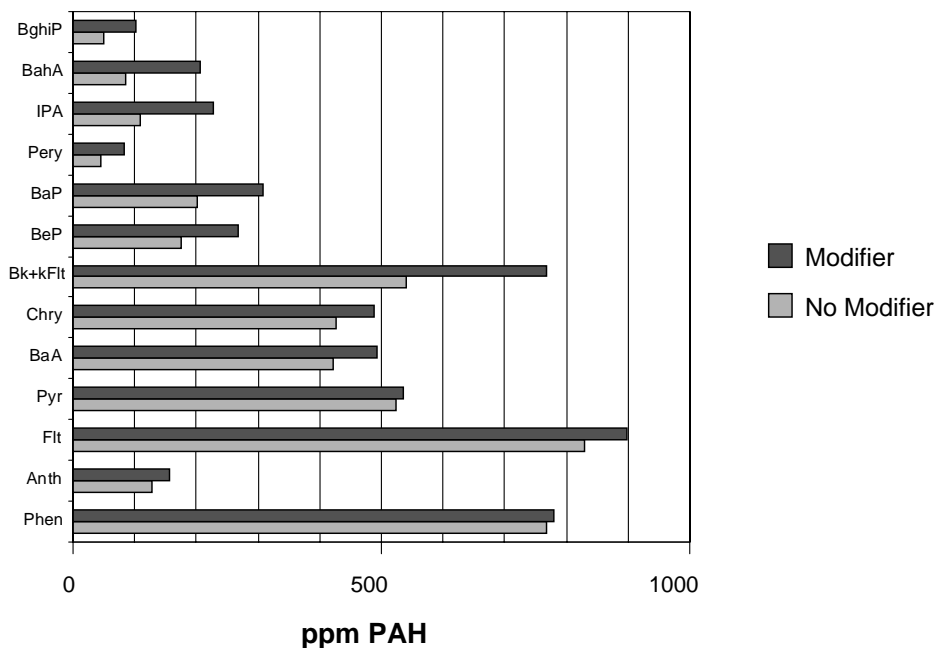


Fig. 1. PAH recoveries in cokery soil by ASE, effect of modifier.

produced good recoveries for most of the compounds with the exception of the six-ring PAHs. As expected from thermodynamic considerations, higher temperatures resulted in better extraction efficiency for these high molecular weight PAHs. However, 150 °C did not result in significantly higher recovery.

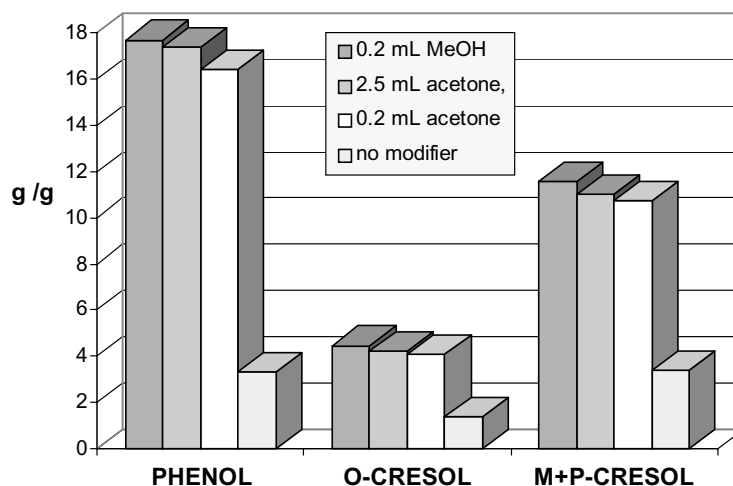


Fig. 2. Phenol recoveries by ASE, effect of modifiers.

Table 1  
PAH recoveries from SRM 1649 at various temperatures

	Recoveries (%)		
	50 °C	100 °C	150 °C
Phenanthrene	78.6	90.7	95.9
Fluoranthrene	92.6	89.7	92.9
Pyrene	85.2	77.5	84.0
Benz( <i>a</i> )anthracene	81.0	81.5	88.0
Chrysene	112.3	118.0	126.0
Benzo( <i>b,k</i> )fluoranthene	100.7	105.2	107.5
Benzo( <i>a</i> )pyrene	77.4	80.6	73.9
Benzo( <i>g,h,i</i> )perylene	66.9	76.6	75.4
Indeno(1,2,3- <i>cd</i> )pyrene	65.6	79.2	74.5

We also studied the influence of the temperature in the extraction of phenols from the cokery soil with 18% carbon content. Extractions were carried out at 100 and 150 °C while keeping the rest of the extraction parameters the same. As can be seen in Fig. 3, higher temperature was necessary for this more adsorptive matrix: the amount of phenols found at 100 °C were only 70–80% of that obtained at 150 °C.

As expected, the optimum extraction temperature depends on the type of compounds as well as on the matrix but, as we have demonstrated, extraction temperatures between 100 and 150 °C are high enough to give good recoveries in most cases.

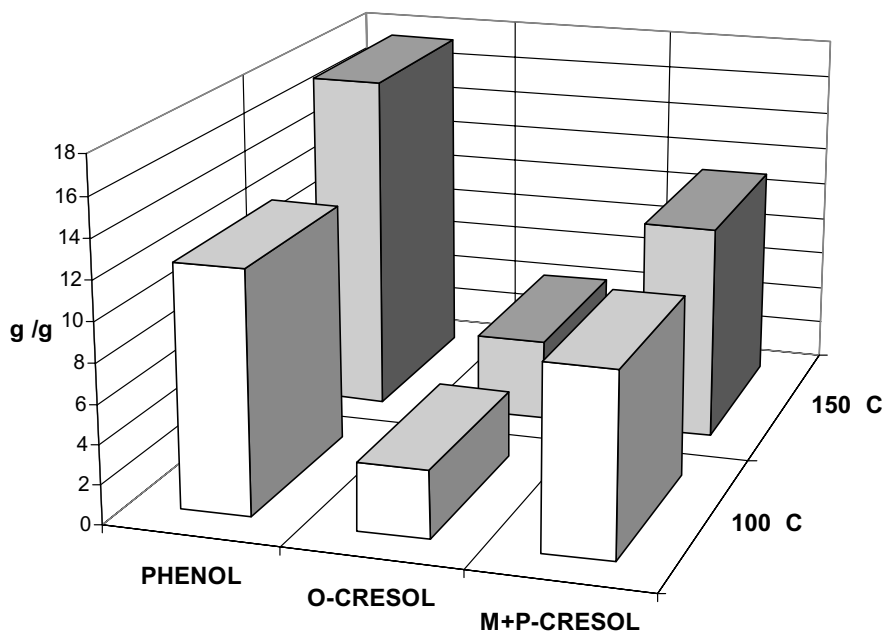


Fig. 3. Phenol recoveries by ASE at different temperatures.



Table 2  
Hydrocarbon recoveries from diesel-contaminated soil (triplicate determinations)

	Sonication	MAP <sup>TM</sup>	ASE
Mean recovery ( $\mu\text{g/g}$ )	2166	2582	2727
R.S.D. (%)	8.3	5.3	8.9

### 3.4. Degradation of thermally labile pollutants

Because of the high temperature and pressure required in ASE, degradation of some compounds might occur [13]. To study this effect, the DDT and endrin pair were used. The pesticide DDT is known to degrade to DDD and DDE, whereas endrin to endrin aldehyde and endrin ketone at high temperature in the presence of active sites. These compounds were spiked onto a glass-fibre filter at 0.2 mg per filter and extracted at 150 °C and 100 atm for 30 min to accentuate any degradation effect that might occur. The extract volume was reduced to 10-ml and analysed on the GC/MSD operated in scan mode. The spiking solution containing the pair of pesticides at 20 ng/ml was injected to provide a basis for comparison. Results show that after ASE, DDD was present at 5.5% of DDT and endrin ketone at 5.3% of endrin. The extent of degradation was actually less than that of the standard injection in which DDD was present at 9.4% of DDT and endrin ketone at 6.4% of endrin (presumably at the heated injection port of the GC). Instrument variation was thought to be the cause of discrepancy because the analytes were near the detection limit of the MSD in scan mode (about 0.2 ng/ml).

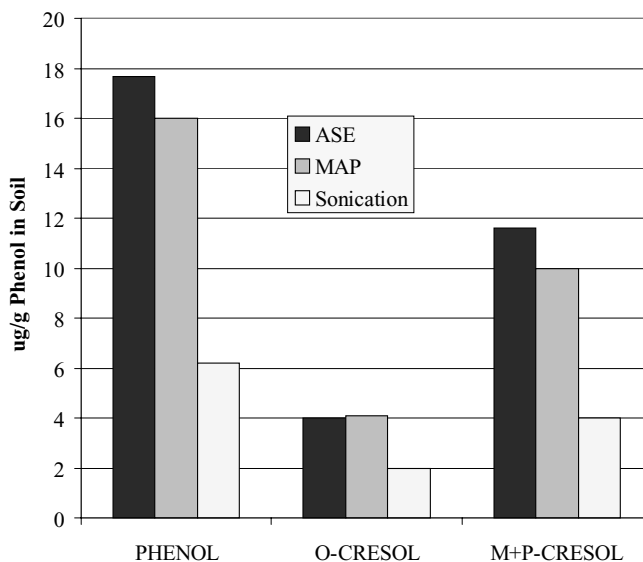


Fig. 4. Phenol results in cokery soil by three extraction methods.

Table 3  
PAH results of SRS 103-100 certified reference material by ASE four determinations

	Reference value ( $\mu\text{g/g}$ )	Confidence interval	Measured value ( $\mu\text{g/g}$ )	Recovery (%)	R.S.D. (%)
Anthracene	431	389.1–473.2	392.6	91	9.3
Phenanthrene	1925	1716.2–2133.6	1620.9	84	12.0
Fluoranthene <sup>a</sup>	1426		1300.5	91	10.9
Pyrene	1075	933.9–1216.3	1155.6	108	10.9
Benzo( <i>a</i> )anthracene	264	240.8–288	244.7	93	6.8
Chrysene	316	286.5–345.8	327.4	104	10.0
Benz( <i>b,k</i> )fluoranthene <sup>a</sup>	178.4		207.5	116	11.7
Benzo( <i>a</i> )pyrene	97	84.7–108.3	112.8	116	11.2
Benzo( <i>g,h,i</i> )perylene <sup>a</sup>	25.5		33.7	132	8.7
Indeno(1,2,3- <i>cd</i> )pyrene	32	23.9–40	31.2	97	6.6
Dibenzo( <i>a,h</i> )anthracene <sup>a</sup>	14.2		12.1	85	8.6

<sup>a</sup> Compounds with non-certified value.

### 3.5. Comparison with sonication and MAP<sup>TM</sup>: validation of the method

While Soxhlet extraction is the accepted method for soil extraction, field work in a mobile laboratory generally precludes its use because of the requirement of cooling water in the condensers. ASE is attractive as a rapid field extraction technique and uses minimum amount of solvent. Other candidate field extraction techniques were investigated which include ultrasonic extraction and closed-vessel MAP<sup>TM</sup> extraction [14]. These studies were conducted with actual soils with three different classes of contaminants. The first one was a diesel contaminated soil from a gas process plant, the other was a cokery soil heavily contaminated with PAH and phenol.

The results obtained for the extraction of diesel hydrocarbon are shown in Table 2. ASE and MAP<sup>TM</sup> gave similar recoveries. The recoveries obtained with sonication were slightly lower at about 80% of the ones obtained with the other two techniques.

The results obtained for the extraction of phenols in cokery soil are shown in Fig. 4. Again ASE and MAP<sup>TM</sup> gave essentially identical recoveries. Sonication was found to

Table 4  
PAH results of SRM 1649 urban dust by ASE four determinations

	Reference value ( $\mu\text{g/g}$ )	Measured value ( $\mu\text{g/g}$ )	Recovery (%)	Precision (%)
Phenanthrene <sup>a</sup>	4.5	4.3	94	6.8
Fluoranthene	7.1 $\pm$ 0.5	6.4	90	6.4
Pyrene <sup>a</sup>	6.6	5.6	84	9.8
Benzo( <i>a</i> )anthracene	2.6 $\pm$ 0.3	2.3	88	9.3
Chrysene <sup>a</sup>	3.6	4.5	126	7.1
Benz( <i>b,k</i> )fluoranthene <sup>a</sup>	8.2	9.0	109	5.2
Benzo( <i>a</i> )pyrene	2.9 $\pm$ 0.5	2.3	80	5.8
Benzo( <i>g,h,i</i> )perylene	4.5 $\pm$ 1.1	3.4	76	1.7
Indeno(1,2,3- <i>cd</i> )pyrene	3.3 $\pm$ 0.5	2.5	76	4.6

<sup>a</sup> Compounds with non-certified value.

be inadequate for the extraction of phenol and cresols in this highly sorptive matrix, and the recoveries obtained were only 50% of the ones with ASE and MAP<sup>TM</sup>.

The three techniques showed similar precision, with an average R.S.D. of 8%. The ASE method was also validated with two different certified materials, SRM 1649 urban dust and SRS 103-100 certified reference material. The PAH results are shown in Tables 3 and 4. ASE produced recoveries over 75%. High recoveries were obtained for some compounds, for which reference values are not available. Even without clean-up, the peaks were reasonably sharp and the high temperature/pressure environment did not seem to extract more background material in comparison to conventional techniques.

#### 4. Conclusion

Although we have not covered all classes of environmentally-important compounds, ASE of representative semi-volatile compounds in different artificial matrices as well as real samples indicate this technique is a viable technique among the new regime of rapid and low solvent consuming extraction methods such as MAP<sup>TM</sup>. Recoveries using ASE extraction were in all cases satisfactory, offering good agreement with the certified values and also comparable with the results obtained using closed-vessel MAP<sup>TM</sup> extraction. These techniques have shown to be more powerful than ultrasonic extraction. Savings in time, solvent usage and labour are possible due to the high extraction efficiencies at high temperature/pressure conditions. An added advantage of ASE is the significantly shortened method development time because the same solvent used in existing extraction methods can be used, reducing the amount of time for method optimisation.

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