Ultrasound-assisted pressurized solvent extraction for aliphatic and polycyclic aromatic hydrocarbons from soils

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Abstract

In the present work the efficiency of extraction of aliphatic diesel range organics (DROs) and polycyclic aromatic hydrocarbons (PAHs) from soil was assessed by using dynamic modes of pressurized solvent extraction (PSE), and ultrasound-assisted pressurized solvent extraction (US-PSE). Optimization studies were carried out using a blank soil (Non-Polluted Soil#1, CLN-1, RTC) and a real soil which was previously spiked with the analyte mixture and aged for 90 days. A laboratory-made manifold with controlled temperature and pressure was used to carry out the leaching processes. The extraction cell was inserted into an oven for PSE and into an ultrasound bath for US-PSE. The following variables were studied in each case, keeping the pressure at about 1800 psi: extraction temperature, time of static and dynamic extraction and solvent flow rate. In addition, the time of ultrasound application was also studied in US-PSE. For PSE with dichloromethane (DCM) the recoveries were about 90–95% for both the families of analytes, using extraction times of 20 min. Analyte extraction was quantitative by using US-PSE with DCM for 10 min. In all cases, after the extraction process, the analytes were determined by GC–MS. Application of the method to a natural contaminated sample suggests that either the extraction time used in US-PSE should be increased to 20 min or the solvent (DCM) should be replaced by a mixture of DCM:acetone (1:1), to reach comparability with Soxhlet extraction.

1. Introduction

In addition to physical impacts of petroleum spills, the toxicity of many of the individual compounds contained in petroleum is significant, and even small releases can kill or damage organisms from the cellular- to the population-level. Compounds such as polycyclic aromatic hydrocarbons (PAHs) are well-known human carcinogens and occur in varying proportions in crude oil and refined products. Making informed decisions concerning ways to determine the fate and effects of petroleum spills requires high-quality data and analytical tools for rapid production of opportune information.

The analytical determination of organic pollutants such as aliphatic and aromatic hydrocarbons in solid matrixes (for instance, soils and sediments), usually presents extensive and complex operations of sample preparation, mainly due to the difficulty of quantitatively leaching the analyte from the solid sample. Because in some occasions the interactions established between analytes and solid matrix are very strong, the traditional methodologies based on Soxhlet extraction do not provide enough energy to release the analytes rapidly, thus requiring very long extraction times (8–48 h).

A number of modern solid–liquid extraction techniques have been described in recent years in an attempt to increase extraction efficiency, decrease the organic solvent consumption and increase sample throughput [1–19].

A comparison between Soxhlet extraction, pressurized solvent extraction (PSE), subcritical water extraction (SWE) and supercritical fluid extraction (SFE) has been previously carried out by Hawthorne et al. [1] for the extraction of PAHs from PAH-contaminated soils and for the extraction of alkanes and PAHs in urban air particulate matter [1,2]. With SWE, PAHs were efficiently extracted (1 h at 250 °C, 30 min at 300 °C) in urban particulate matter with little or no extraction of alkanes. Soxhlet and PSE extract both the families of compounds in 18 h and 50 min, respectively and SFE, due to the very low polarity of

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CO_2, first extracts the bulk alkanes in mild conditions, followed by stronger conditions to extract the remaining PAHs. A similar situation was observed in the airborne particulate matter of Santiago de Chile [3] in which SWE was applied, but extraction of PAHs was only quantitative for PAHs of molecular weight lower than 200. In these studies, ultrasound (US) was not used to assist the extractions.

The analytical uses of ultrasound in sample preparation have been recently reviewed by Priego-Capote and Luque de Castro [4]. Particularly interesting is the fact that US has been applied to assist other current extraction options, such as SFE and Soxhlet extraction. In the former case, an US transducer was installed inside the extractor [5] and in the latter, US was applied in the cartridge zone before siphoning of the Soxhlet [6]. In contrast, pressurized solvent extraction has also been assisted by ultrasound for the extraction of organophosphate esters in air samples [7,8].

In the present study, PSE and ultrasound-assisted pressurized solvent extraction (US-PSE) were assessed for extraction of aliphatic diesel range organics (DROs) and aromatic hydrocarbons from soil. Soxhlet extraction was used as a reference technique, for comparison.

2. Experimental

2.1. Reagents

De-ionized water (NANOpure ultrapure water system; Barnstead, Dubuque, IA, USA) was used throughout. Working standard solutions of PAHs were prepared by dilution of an EPA 610 Polynuclear Aromatic Hydrocarbons Mix containing concentrations from 100 to 2000 µg/ml (SUPELCO Park, Bellefonte, PA, USA, 4-8743). Working standard solutions of DROs were prepared by dilution of a 1000 µg/ml solution (Chem Service Inc., West Chester, PA USA, TPH-6RPM). A mixed standard solution prepared in Dichloromethane (GC–MS/Pesticides grade analysis, Fisher Scientific, Fair Lawn, NJ, USA), was used both to spike the soils and for calibration purposes. During each sequence of sample analysis, linearity was checked by including the mixed standard solutions in the sequence. Dichloromethane (DCM) was used in PSE and US-PSE extraction and as a final extractant in SWE. A certified reference material Non-Polluted Soil CLN SOIL#2 (manufactured by Resource Technology Corp., Laramie, WY 82073, USA) was spiked at a level of 10 mg/Kg and used to optimize the different extraction procedures.

2.2. Instruments and apparatus

The schematic build-up of the extraction unit is shown in Fig. 1. All the tubing (1/16″, 1/8″ O.D.) was made of SS 306 stainless steel. Connections were made using Swagelok fittings (Solon, OH, USA). The following valve type was employed: Swagelok needle valve SS-ORS2 (5000 psi allowed pressure).

The extraction chamber for PSE consisted of a laboratory-made oven (a $28\,cm \times 12\,cm \times 5\,cm$ aluminum block with controlled temperature). A temperature controller BTC-704-41521000; Spec.: J, 0–400 °C (Brainchild Electronic Co. Ltd., Taipei, Taiwan) was used to maintain the temperature at the desired value. Inside the chamber a preheated coil (2 m stainless steel tube SS-316, 1/16″, 0.1 mm I.D., Supelco, Bellefonte PA, USA) was located to keep the programmed temperature and was followed by the extraction cell (a 12 mm I.D. empty HPLC column, Supelco, Bellefonte PA, USA). In the case of US-PSE the oven was replaced by an ultrasonic bath (Elma, Model Transsonic Digital D-78224 Singen/Htw, Übach-Palenberg, Germany) with programmable temperature. The solvent used for the extractions was pumped using an HPLC pump (Perkin-Elmer series 200, Wellesley, MA, USA). For extraction, the working range of pressure inside the system was kept at 1800 ± 50 psi.

Quantitation was performed using a gas chromatograph Hewlett-Packard model 5890 series II coupled to a mass selective detector Fisons Instruments model MD 800.
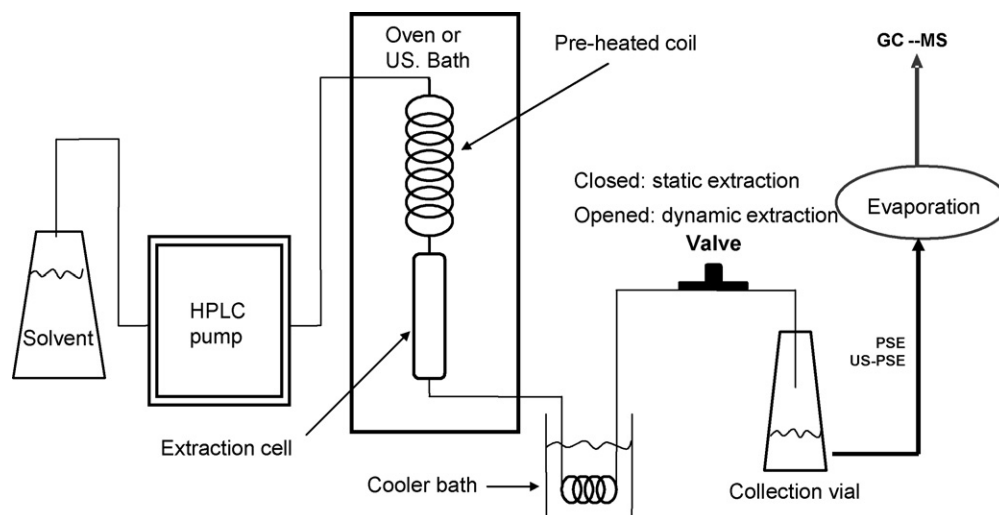

Fig. 1. Extraction manifold for implementation of the methods (SWE, PSE and US-PSE).

2.3. Spiking procedure

For optimization of variables and recovery studies a blank soil (Non-Polluted Soil#2, CLN-2, Resource Technology Corp., Laramie, WY 82073, USA) and a real Alfisol soil from the VI region of Chile were considered. The latter soil contains 8.6% organic matter, 26.6% clay, 14.0% silt and 59.4% sand. Spiked soil preparation was made by diluting a stock mixture of the hydrocarbon standard in 250 ml of DCM and mixing in amber bottles with 200 g of soil to obtain a final concentration of 10 mg/Kg. The bottles were placed in a hood, and the solvent was slowly evaporated with constant stirring. The spiked soils were aged for 90 days at room temperature and thereafter stored at 4 °C.

2.4. General analytical procedure

The spiked soil and real soil samples were separately extracted according to the following procedures:

2.4.1. Pressurized solvent extraction

Samples (500 mg) were weighed and loaded into an extraction cell located inside the aluminum chamber–oven extractor. The oven was coupled to a heating device located on the upper part of the chamber and electronically controlled through a thermocouple to reach the desired temperature (300 °C). The temperature of the oven was checked monthly with an external probe (Digi-Sense Thermocouple Thermometer EW-93000-00, Cole Parmer, Vernon Hills, IL, USA). Then, DCM was pumped through the system (dynamic extraction) to extract the analytes from the soils at a flow rate of 1 ml/min for 20 min. After PSE was done, the extract was characterized by GC–MS. The solvent was evaporated to 2 ml prior to injection. Optimization of the extraction considered the following variables: extraction temperature, static and dynamic extraction time, and flow rate of the solvent.

In each set of experiments one blank was always processed and one standard was injected to check the linearity. All the samples were processed in triplicate.

2.4.2. Ultra-sound assited pressurized solvent extraction

The same procedure and manifold implemented for PSE was used in this case, except that the aluminum oven was replaced by an ultrasonic bath at a temperature of 70 °C. Ultrasound was applied for 5–20 min at 35 KHz. A mixture of methylene chloride/acetone (1:1, v/v) was used in real soil samples. In each set of experiments one blank was always processed and one standard was injected to check the linearity. All samples were processed in triplicate.

2.4.3. Soxhlet extraction

Real soil samples were treated using the conventional Soxhlet extraction procedure. A detailed description of the analytical procedure used for extraction of those samples is described previously [20]. It consists basically of extraction by Soxhlet using methylene chloride/acetone (1:1, v/v) as an extraction solvent system (24 h), and then the extract is characterized by GC–MS after evaporation to 5 ml in a Kuderna–Danish concentrator.

Final determination was carried out in both the extraction alternatives by GC–MS using a HP-5MS fused silica capillary column (30 m × 0.25 mm I.D., and 0.25 μm of film thickness) coated with 5% phenyl–95% methylpolysiloxane. One microliter of sample was injected into the column using splitless mode. The injector temperature was 300 °C. The column temperature was maintained at 40 °C for 2 min, raised up to 150 °C at 15 °C/min, and up to 300 °C at 10 °C/min (6.0 min). A constant flow of 1.0 ml/min of helium as carrier gas was used.

The MS transfer line was held at 280 °C, and quantitations were based on calibration with standard analytes using the mass spectrometric parameters (selected ion monitoring (SIM) mode) shown in Table 1. The first ion mentioned for each analyte in Table 1 was used for quantitation (target ion) and the second one as qualifier. The relative abundance ion ratio should match the comparison standard within ±20%.

2.5. Samples

A soil sample was collected in the V Region (Central Chile) close to the outlet of the Aconcagua river (proximities of

Table 1
Selected target ions and qualifier ions used in selected ion monitoring (SIM) mode

PAH	Retention time (min)	Target-qualifier (*m/z*)	DRO	Retention time (min)	Target-qualifier (*m/z*)
Naphtalene	8.8	127.3–128.9	*n*-Undecane	6.3	56.6–84.8
Acenaphthylene	11.7	150.8–151.6	*n*-Dodecane	7.4	56.6–84.8
Acenaphthene	12.1	152.8–153.8	*n*-Tridecane	8.4	56.6–84.8
Fluorene	13.2	164.8–165.9	*n*-Tetradecane	9.4	56.6–84.8
Phenanthrene	14.5	150.8–175.8	*n*-Pentadecane	10.3	56.6–84.8
Anthracene	14.7	177.8–175.8	*n*-Hexadecane	11.3	56.6–84.8
Fluoranthene	18.2	199.7–201.8	*n*-Heptadecane	12.3	56.6–84.8
Pyrene	18.8	201.5–202.2	*n*-Octadecane	13.3	56.6–84.8
Benzo[a]anthracene	21.8	225.9–227.8	*n*-Nonadecane	14.3	56.6–84.8
Chrysene	21.9	225.9–227.8	*n*-Eicosane	15.3	56.6–84.8
Benzofluoranthene	24.4	251.8–253.0	*n*-Heneicosane	16.2	56.6–84.8
Benzo[a]pyrene	25.1	249.9–251.9	*n*-Docosane	17.1	56.6–84.8
Indeno[1,2,3-c,d]pyrene	28.2	273.9–275.8	*n*-Tricosane	18.0	56.6–84.8
Dibenzo[a,h]anthracene	28.3	275.8–277.9	*n*-Tetracosane	18.9	56.6–84.8
Benzo[g,h,i]perylene	29.1	273.8–275.8	*n*-Pentacosane	19.7	56.6–84.8

the Concón petroleum refinery at 32°55′12.4″ south latitude). Surface (0–10 cm) composed soil samples were collected in polyethylene bags, using an auger. The samples were air dried, ground and sieved (2 mm). All the samples were kept in brown glass brown bottles. The samples were stored at 4 °C prior to analysis.

Samples were analyzed by US-PSE and Soxhlet techniques and comparisons among means were made by using the Tukey procedure (honestly significantly different (HSD)) at 95% level of confidence.

3. Results and discussion

3.1. PSE

By using the manifold depicted in Fig. 1, PSE was assessed for the extraction of the analytes from soils, using dichloromethane as extracting solvent. Extraction temperature was studied in the interval 20–150 °C. Fig. 2 shows an evident increment in extraction efficiency as the temperature increases. A temperature of 100 °C is sufficient to extract PAHs almost quantitatively from soil, whereas in the case of DROs, a temperature of 150 °C is required for quantitative extraction. By keeping a temperature of 100 °C, dynamic time was found quite important for extraction efficiency. As can be seen in Fig. 3, for some representative compounds, in the interval 5–20 min of dynamic extraction both kinds of analytes, PAHs and DROs, are extracted to an almost quantitative extent. The flow rate of dichloromethane was studied from 1 to 3 ml/min. No significant dependence was observed of extraction efficiency on this variable. However, a flow rate of 1 ml/min was selected because at this value better reproducibility was obtained. Under the selected conditions (100 °C, 20 min of dynamic extraction, 1 ml/min flow rate), eight independent extractions were carried out. Precision, expressed as relative standard deviation (RSD), was from 2.4 to 11% for PAHs and from 0.6 to 1.2% for DROs. Recoveries were from 86 to 108% for PAHs and from 89 to 94% for DROs.
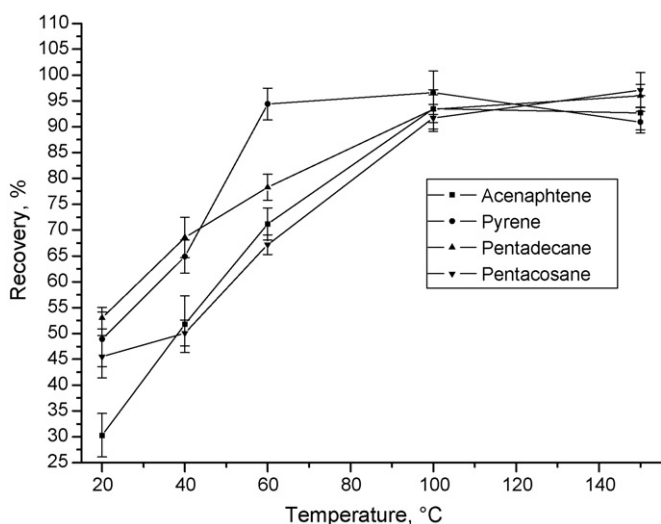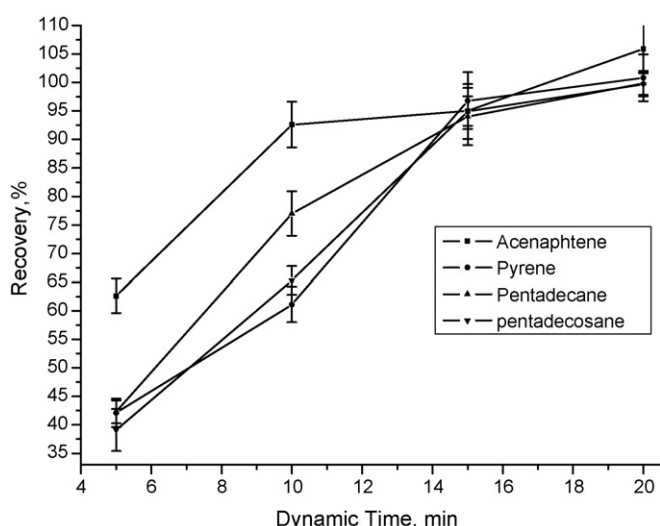

Fig. 3. Effect of dynamic extraction time on the pressurized solvent extraction of hydrocarbons from soil.

The lowest recoveries were observed for the lighter compounds (naphtalene, acenaphtylene, tridecane), which can be related to some volatilization occurring during evaporation of the solvent previous to GC–MS analysis.

3.2. US-PSE

In order to improve the efficiency of pressurized solvent extraction, extraction was assisted by ultrasound. In this case the oven was replaced by an ultrasonic water bath at 70 °C and 35 KHz in which the pre-heater and sample cell were immersed. Higher temperatures were not checked because 70 °C was the maximum temperature allowed used in the bath. The time of ultrasound applied on the sample was assessed from 0 to 10 min, using a dynamic extraction time of 10 min and a flow rate of DCM of 1 ml/min. As can be seen in Fig. 4, ultrasound improved extraction efficiency considerably, and 10 min of

Fig. 2. Effect of temperature on the pressurized solvent extraction of hydrocarbons from soil.
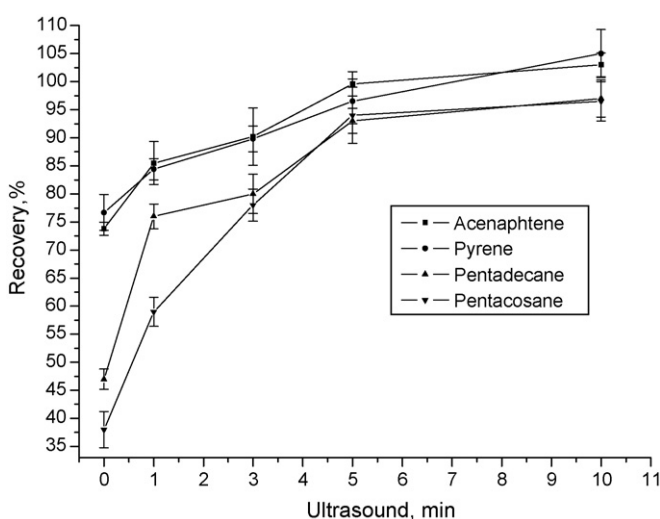

Fig. 4. Effect of time of ultrasound applied on the pressurized solvent extraction of hydrocarbons from soil.

Table 2
Determination of PAHs and DROs in a real soil sample

Analyte	Soxhlet Concentration (mg/Kg ± SD)	US-PSE[a] Concentration (mg/Kg ± SD)	US-PSE[b] Concentration (mg/Kg ± SD)	US-PSE[c] Concentration (mg/Kg ± SD)
Naphtalene	0.12 a ± 0.03	0.09 a ± 0.02	0.12 a ± 0.01	0.12 a ± 0.02
Acenaphthylene	0.10 a ± 0.01	0.08 a ± 0.01	0.10 a ± 0.02	0.11 a ± 0.02
Acenaphthene	0.13 a ± 0.01	0.14 a ± 0.02	0.14 a ± 0.02	0.15 a ± 0.01
Fluorene	0.71 b ± 0.04	0.57 a ± 0.03	0.68 ab ± 0.02	0.74 b ± 0.01
Phenanthrene	0.59 a ± 0.05	0.50 a ± 0.04	0.50 a ± 0.03	0.58 a ± 0.02
Fluoranthene	0.49 a ± 0.02	0.52 a ± 0.04	0.45 a ± 0.05	0.52 a ± 0.03
Pyrene	1.12 a ± 0.09	0.99 a ± 0.04	1.13 a ± 0.03	1.14 a ± 0.04
Benzo[a]anthracene	0.33 a ± 0.08	0.27 a ± 0.01	0.30 a ± 0.05	0.37 a ± 0.05
Chrysene	0.58 c ± 0.07	0.39 a ± 0.01	0.55 ab ± 0.02	0.60 c ± 0.04
Benzofluoranthene[d]	1.36 b ± 0.08	0.91 a ± 0.08	1.10 ab ± 0.06	1.25 b ± 0.05
Sum	5.53 c ± 0.18	4.46 a ± 0.11	5.07 b ± 0.11	5.58 c ± 0.10
n-Undecane	2.1 a ± 0.2	2.4 a ± 0.4	2.0 a ± 0.3	2.2 a ± 0.1
n-Dodecane	3.0 a ± 0.3	2.5 a ± 0.2	2.6 a ± 0.3	3.2 a ± 0.1
n-Tridecane	2.7 a ± 0.6	2.3 a ± 0.5	2.4 a ± 0.5	2.9 a ± 0.3
n-Tetradecane	2.2 a ± 0.08	1.8 a ± 0.1	1.7 a ± 0.3	2.1 a ± 0.5
n-Pentadecane	2.1 a ± 0.1	2.2 a ± 0.3	1.9 a ± 0.3	2.3 a ± 0.1
n-Hexadecane	5.1 a ± 0.6	4.5 a ± 0.8	4.9 a ± 0.2	4.5 a ± 0.2
n-Heptadecane	6.0 a ± 0.4	5.8 a ± 0.3	6.2 a ± 0.3	5.5 a ± 0.5
n-Octadecane	9.4 a ± 0.8	9.0 a ± 0.6	9.5 a ± 0.1	9.5 a ± 0.5
n-Nonadecane	8.8 a ± 0.6	8.5 a ± 0.5	9.0 a ± 0.2	8.4 a ± 0.4
n-Eicosane	10.2 a ± 0.6	9.6 a ± 0.7	9.9 a ± 0.5	9.8 a ± 0.4
n-Heneicosane	10.6 a ± 0.9	9.0 a ± 0.4	10.5 a ± 0.2	9.5 a ± 0.5
n-Docosane	12.8 b ± 0.6	11.3 ab ± 0.7	13.5 b ± 0.3	10.3 a ± 0.5
n-Tricosane	15.2 a ± 2.3	13.7 a ± 1.8	15.5 a ± 0.9	14.0 a ± 0.6
n-Tetracosane	15.2 a ± 1.9	13.4 a ± 1.0	14.9 a ± 0.7	14.0 a ± 1.7
n-Pentacosane	15.9 a ± 1.3	12.8 a ± 0.7	16.6 a ± 1.2	13.8 a ± 1.5
Sum	121.3 c ± 3.8	108.8 a ± 2.8	121.1 c ± 2.0	112.0 b ± 2.7

Same letter in the same row indicate no statistical differences between the means (Multiple Range Test for the Mean, by Tukey procedure (honestly significantly different (HSD)) at 95% level of confidence).

[a] 10 min of dynamic extraction, 5 min of US, DCM as solvent.

[b] 20 min of dynamic extraction, 20 min of US, DCM as solvent.

[c] 10 min of dynamic extraction, 5 min of US, DCM:acetone (1:1) as solvent.

[d] Sum of benzo[b]fluoranthene plus benzo[k]fluoranthene.

dynamic extraction is quite satisfactory for quantitative extraction of both the families of analytes. Under these conditions, the time of extraction can be reduced by a half compared with pressurized solvent extraction without ultrasound assistance.

Once the variables with the spiked certified non-polluted soil were optimized, extraction of the spiked analytes was carried out on the real spiked soil. The repeatability of the method was assessed by processing eight samples of the spiked real soil under the selected conditions. Relative standard deviation of the determinations was in the range 4.2–9.1% for PAHs and 0.8–6.8% for DROs and recoveries were from 94 to 103% for PAHs and from 96 to 98% for DROs. The detection limits of the method for the analytes, defined at a signal-to-noise ratio of 3, were between 9.6 and 30.6 µg/kg for PAHs and between 59.8 and 203.2 µg/kg for DROs.

3.3. Analysis of real soil samples

In order to demonstrate the usefulness of the US-PSE method, this was applied to the determination of the analytes in a real soil sample collected in the V Region (Concón) of Chile close to the outlet of the Aconcagua River ($32°55'12.4''$ south latitude). Very near to this place is located a big crude oil refinery. The sample was also subjected to Soxhlet extraction for comparison. The results obtained for both the methods are shown in Table 2.

As can be seen in the table, 11 PAHs and 15 DROs could be identified. In general it is possible to observe that the concentrations obtained (column 3, Table 2) are slightly lower in the case of US-PSE compared to Soxhlet (column 2, Table 2) and according to the Tukey procedure (honestly significantly different test), at 95% level of confidence, the sum of concentrations of both PAHs and DROs are statistically different in both cases. The precision is quite comparable in both extraction techniques. Soil is a complex matrix of inorganic and organic constituents and its composition drives contaminant mobilization in a soil matrix. The specific portion of the soil with which a contaminant interacts will depend on both the compound and the matrix, as well as on the time of contact between them. In this context, one more time it is demonstrated that the most realistic situation for evaluation of an extraction technique is the use of a native contaminated soil. However, since it is practically impossible to find a natural matrix contaminated with all the analytes under study, the use of a spiked soil that has been allowed to age appears as a good model for evaluation

of the leaching technique. This fact can partially explain the observed differences between Soxhlet extraction and US-PSE, indicating that the conditions selected for spiked samples are not sufficient for natural contaminated samples. Consequently, the sample was subjected to US-PSE again under the same conditions, but the time of application of ultrasound was increased to 20 min. As can be seen in Table 2 (column 4), the results obtained under these conditions are more comparable to Soxhlet, the sum of concentrations of DROs being statistically equivalent in both techniques. In contrast, it is well documented that for the extraction of low-polar microcontaminants from highly complex matrices, mixtures of apolar–polar solvents (as the one used for Soxhlet extraction) have typically provided higher extraction efficiencies than apolar solvents (such as dichloromethane, used for US extraction). Following the implications of these considerations and according to data reported in Table 2, one could conclude that dichloromethane may not be the optimum selection for this type of application. Hence, the same experiment was made but using the same solvent mixture as for Soxhlet extraction: DCM:acetone (1:1). As can be seen in Table 2 (last column), the concentrations obtained are also comparable to those obtained by Soxhlet, in this case the sum of concentrations of PAHs being statistically equivalent in both cases. This confirms the fact that a mixture of apolar and polar solvents also provides more efficiency in US-PSE, particularly in the case of PAHs.

4. Conclusions

In the present study the optimization of variables associated with the extraction of diesel organic range aliphatic and polycyclic aromatic hydrocarbons from soil was assessed by using dynamic modes of PSE and US-PSE.

Recoveries were determined by analysis of spiked real soils. For PSE with dichloromethane the recoveries were about 90% for both the families of analytes, using extraction times of 20 min. In contrast, the extraction of the analytes was quantitative by using US-PSE with DCM for 10 min.

When US-PSE was compared with Soxhlet extraction in a real contaminated sample, the results provided by the proposed method were statistically lower that those obtained by the conventional Soxhlet method, indicating that, in real samples, either the time of US should be increased or mixtures of apolar–polar solvents should be used. However, when a critical comparison

is established between the proposed extraction methods and the conventional Soxhlet extraction method, it should be considered that: (a) extraction time is decreased from 20 h to less than 1 h; and (b) the organic solvent used in the extraction procedure can be decreased to less than 5%.

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