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Short communication

Pressurised liquid extraction of ketones of polycyclic aromatic hydrocarbons from soil

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Abstract

Pressurised liquid extraction (PLE) was used in the extraction of three ketones of polycyclic aromatic hydrocarbons from the sample of a soil highly contaminated with polycyclic polyaromatic compounds. The choice of solvent was the only factor that considerably influenced the extraction efficiency of PLE under the conditions recommended in Method 3545A promulgated by the United States Environmental Protection Agency. The dichloromethane–ethanol solvent mixture was found to be the most efficient solvent. PLE using this mixture provided better recoveries of all analysed ketones relative to Soxhlet extraction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

An extraction is usually the first step in analytical procedures applied to the determination of organic compounds in solid matrices. The use of a convenient type of extraction not only influences the accuracy of results, but also determines the total analysis time and in this way affects sample throughput and analysis costs.

Several efficient extraction techniques have been developed and are commonly used for analyte isolation from solid matrices. Soxhlet extraction is still mostly used in laboratory practice as a part of many analysis protocols due to high extraction efficiency,

but the method is time consuming and solvent volumes are relatively large. Other frequently employed extraction methods include an automated form of Soxhlet extraction [1], sonication [2], microwave extraction [3], supercritical fluid extraction (SFE) [4–6] and pressurised liquid extraction (PLE).

The use of solvent under elevated, but subcritical temperatures (up to 200°C) and pressures (up to 20.7 MPa) was introduced by Dionex in 1995 [7,8] as accelerated solvent extraction (ASE).

PLE was successfully used in the extraction of polynuclear aromatic hydrocarbons [9–12], chlorinated biphenyls [13,14], pesticides [15–17], organotin [18], anionic surfactants [19], polymer additives [20], etc., from various solid matrices. Good efficiency, combined with short extraction time, small consumption of organic solvent, easy operation and automation of this technique resulted

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in the fast recognition of PLE by the United States Environmental Protection Agency (EPA) [21].

Ketones of polynuclear aromatic hydrocarbons (keto-PAHs) are among a group of PAH derivatives which became ubiquitous in the environment. Their more polar character (relative to parent PAHs) often makes their extraction more difficult than that of non-derivatized PAHs. This fact, together with the toxicity of these compounds, highlighted the need for reliable analytical methods for their determination [22–24].

In this work, the extraction efficiency of PLE was investigated for the extraction of selected keto-PAHs from a real soil sample.

2. Experimental

2.1. Sample

The sample of soil was taken from the shoulder of road No. II/437 (Leg Týn-Lipník, Czech Republic) and was dried at room temperature (48 h). After the removal of larger vegetation debris, the soil was ground and the powdered soil was sieved through an 80-mesh screen. Finally, the sieved soil was homogenised by mixing for 1 h. The prepared sample of soil was stored in the dark at room temperature.

To minimise the influence of possible changes to keto-PAH content during comparative measurements of extraction efficiency, PLE and Soxhlet extraction were always performed simultaneously.

All organic solvents used in this work were analytical grade or better.

2.2. Extraction techniques

2.2.1. Soxhlet extraction

A classic Soxhlet apparatus and a mixture of dichloromethane–acetone (1:1, v/v), or dichloromethane–ethanol (1:1, v/v), was used for Soxhlet extraction of keto-PAHs (other conditions in Table 1). To prevent the transfer of solid particles to the solvent, the sample was wrapped in filter paper during extraction. After extraction, the solvent was evaporated to the required volume (approx. 25 ml) and the internal standards were added before analysis.

2.2.2. Pressurised liquid extraction

All PLE experiments were made by use of a Fastex 01 apparatus (Applied Separations, Allentown, PA, USA). An extraction vessel with an inner volume of 11 ml was used. This instrument enabled a fully automated operation, other than insertion of the vessel into the oven block and tightening of the cap. All extraction parameters (pressure, temperature, duration of static extraction period and solvent flushing, number of static extraction periods, etc.) were adjusted by means of instrument software.

The standard conditions of PLE for the extraction of polycyclic aromatic compounds according to EPA Method 3545A [21] were initially chosen. The final conditions are given in Table 1. To prevent clogging of the metal frit at the exit of the extraction cell, the frit was separated from the sample by filter paper. A circle of filter paper was also put on top of the soil layer. Nitrogen was used for flushing solvent out of the cell. Solvent was collected in a 40-ml vial and

Table 1
Conditions of extraction techniques

	Soxhlet	PLE
Amount of sample (g)	1.5	1.5
Extraction medium	Organic solvent	Organic solvent
Volume of organic solvent (ml)	250	25
Extraction temperature (°C)	b.p. of solvent	100
Extraction pressure (MPa)	Atmospheric	15
Extraction time	16 h	2×5 min
Pre-heat period (min)	–	5 (1)
Nitrogen purge (min)	–	1 (1)

taken for analysis without any treatment (other than the addition of internal standards).

2.3. Gas chromatographic–mass spectrometric analysis

All extracts were analysed on a gas chromatograph GC 8060 connected to a mass spectrometer Trio-1000 (Fisons, Manchester, UK).

The gas chromatograph was equipped with a 1.5 m×0.32 mm deactivated fused-silica guard column connected to a 007-5MS fused-silica capillary column (30 m×0.18 mm, film thickness 0.25 μm) from Quadrex (New Haven, CT, USA). The carrier gas was helium at a linear velocity of 35 cm/s (at 50°C). A sample volume of 1.0 μl was injected into a split–splitless injector, operated in the splitless mode (splitless time: 50 s) at a temperature of 280°C.

The temperature program was started at 40°C for 1 min. Subsequently, the temperature was increased to 140°C at 10°C/min and then without delay to 295°C at 7°C/min. The temperature of 295°C was held for 20 min. The temperature of the gas chromatography–mass spectrometry (GC–MS) system interface was 295°C.

Electron ionization under standard conditions (70 eV electrons) was used for mass spectrometric analysis (EI+). The temperature of the ion source was 230°C.

Mass spectra for identification of keto-PAHs were obtained in the scan mode (mass range: m/z 40–300, scan time: 1 s). The keto-PAHs in the sample were identified by comparison of their measured spectra and retention times with those of standard compounds.

Selected-ion monitoring of positive ions was used for quantification (dwell time and interchannel delay were 0.08 and 0.02 s, respectively). The molecular ions of 9-fluorenone, 9,10-anthracenedione and 7H-benz[de]anthracen-7-one (m/z 180, 208 and 230, respectively) were monitored for quantification. Typical $[M-28]^+$ ions (m/z 152, 180 and 202, respectively) as well as retention times were used for compound confirmation.

The quantification of keto-PAHs was based on an internal standard calibration method [25]. [$^2\text{H}_{10}$]Phenanthrene and [$^2\text{H}_{12}$]perylene were used as internal standards.

3. Results and discussion

A real sample of soil was subjected to PLE with the aim of finding conditions under which this extraction technique would achieve an extraction efficiency comparable with the Soxhlet extraction of selected ketones of polycyclic aromatic hydrocarbons, 9-fluorenone (9-FO), 9,10-anthracenedione (9,10-ADO) and 7H-benz[de]anthracen-7-one (7-BAO). This soil sample was highly contaminated with PAHs originating from traffic pollution [26] and these ketones were only minor components of the extracted complex mixture. Their concentrations determined in Soxhlet extracts were 8.20, 18.44 and 9.32 μg/g, for 9-FO, 9,10-ADO and 7-BAO, respectively. The relative standard deviations (RSDs) of six determinations were in the range of 4.0–6.1%. To exclude possible losses of analytes in subsequent procedures, all samples were analysed without any clean-up step. The only treatment of the extracts was the evaporation of the Soxhlet extracts to a volume comparable with the volume of PLE extracts.

The PLE conditions for the extraction of semivolatile organics according to EPA Method 3545A [21] were initially used. Under these experimental conditions with dichloromethane–acetone (1:1, v/v) as an extraction solvent, the recovery of 9-FO was comparable with that of Soxhlet extraction. Extraction efficiencies of about 90% and 80% were obtained for 9,10-ADO and 7-BAO, respectively.

Subsequently, size of sample, influence of time of static extraction, effect of extraction solvent and temperature effect were tested.

Sample sizes in the limited mass range of 0.5–3.0 g (in 0.5 g increments) were examined. PLE efficiency for keto-PAHs was not changed in this range and a mass of 1.5 g was used for the rest of the experiments. This amount of sample allowed for the proper quantification of keto-PAHs without evaporation of final PLE extracts.

The duration of extraction was tested in two steps. Firstly, the time of static extraction period was increased, and secondly, the sample was subjected to repeated extraction.

Three different times (5, 10, 15 min) were used for a single static extraction period. This prolongation of the period had no influence on the extraction

efficiency of keto-PAHs. Subsequently, up to three repeated static periods were applied to the sample. The times of the static periods were 5, 10, 15 min. Fresh solvent was used for each extraction period. In all cases, extracts of the second period contained about 3% of 9-FO and 9,10-ADO. No detectable amounts of keto-PAHs were found in extracts after the third static period. The small increase in extraction efficiency was probably caused by the use of fresh solvent rather than by the extension of extraction time of subsequent extractions. In spite of the main portion of analytes being extracted in the first 5-min extraction, two 5-min static extractions per sample were used in further experiments. These results are in agreement with previously published data [9,14].

To improve the recovery of 9,10-ADO and 7-BAO, several organic solvents other than dichloromethane–acetone (1:1, v/v) were tested for PLE under the conditions presented in Table 1. Toluene, dichloromethane and acetone were chosen because of their good extraction capabilities for PAHs [9,11]. Hexane was chosen for the evaluation of the recovery decrease in the case of non-polar solvent for

the extraction of keto-PAHs. The results are given in Fig. 1.

With individual solvents, the highest recoveries (above 90% for all keto-PAHs) were obtained with dichloromethane. The loss of PLE efficiency with hexane was about 60% for 9-FO and greater than 80% for 9,10-ADO and 7-BAO relative to the Soxhlet extraction. The difference in the average recovery of keto-PAHs between PLE with the dichloromethane–acetone mixture and PLE with hexane was 65%, while a recovery decrease of 16% was reported for the sum of 16 selected PAHs for these extraction solvents under similar conditions [11].

Subsequently, non-toxic ethanol was used as an example of a more polar organic solvent for extraction. Despite the fact that PLE ethanol extracts contained precipitates after cooling to room temperature, the efficiencies for all keto-PAHs were comparable with those obtained by Soxhlet extraction. To solve the precipitation problem, a dichloromethane–ethanol (1:1, v/v) mixture was chosen, and the recoveries of 107.8, 111.6 and 103.6% (average value of five extractions) were obtained for 9-FO, 9,10-ADO and 7-BAO, respectively (Fig. 1). The

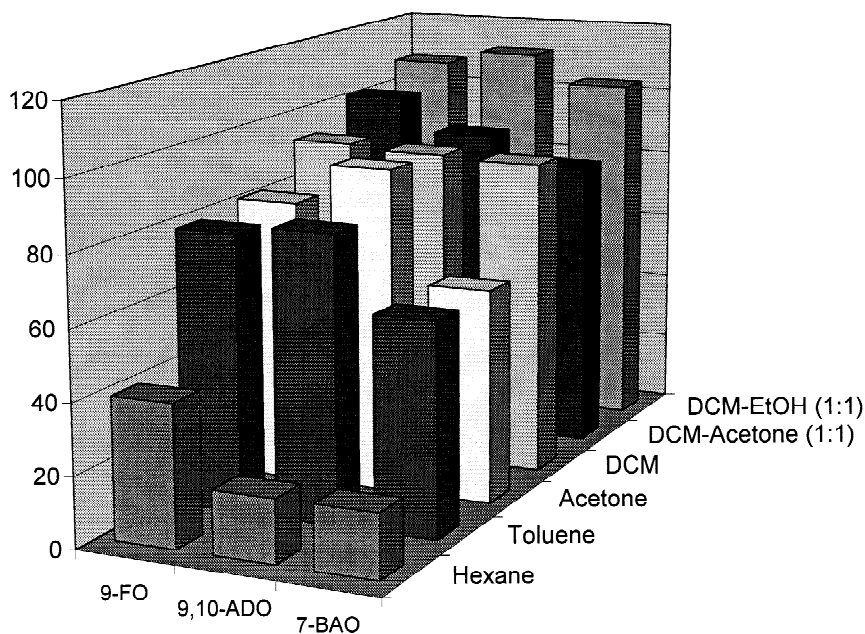


Fig. 1. Extraction efficiency of PLE with different solvents. DCM and EtOH are dichloromethane and ethanol, respectively. Recovery of Soxhlet extraction was taken as 100%, average recovery values of three extractions were used.

Table 2
Temperature effect on PLE recoveries^a

Temperature (°C)	Recovery (%)		
	9-FO	9,10-ADO	7-BAO
100	101.3	104.0	106.6
125	110.0	102.1	110.6
150	128.0	107.2	115.5
175	203.3	109.7	117.0
195	207.5	105.6	103.2

^a Recovery of Soxhlet extraction was taken as 100%, extraction solvent was dichloromethane–ethanol (1:1, v/v), average recovery values of three extractions were used.

RSDs of five determinations were in the range of 3.5–5.9%.

The temperature effect on PLE recoveries was investigated with a mixture of dichloromethane–ethanol (1:1, v/v) in the temperature range of 100–195°C (other conditions according to Table 1). While recoveries of 9,10-ADO and 7-BAO remained approximately the same in this temperature range, the recovery of 9-FO increased with higher temperatures (Table 2). This increase in 9-FO recovery was probably caused by coelution with any substances which may have been extracted only at higher temperatures, even if the mass spectrum of 9-FO peaks in those extracts seemed to be clear. The influence of increased temperature (up to 150°C) was investigated for PLE with the dichloromethane–acetone mixture, but recoveries of keto-PAHs were not increased relative to those obtained at a temperature of 100°C.

4. Conclusions

PLE proved to be a suitable technique for the extraction of keto-PAHs. Recoveries of the examined keto-PAHs obtained by PLE were better than those observed by Soxhlet extraction, when a mixture of dichloromethane–ethanol (1:1, v/v) was used. The reproducibility of PLE (RSD up to 6%) was comparable to that of Soxhlet extraction.

Under the conditions proposed in EPA Method 3545A, the only parameter which considerably influenced the recovery (mainly for 9,10-ADO and 7-BAO) was the extraction solvent.

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