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# MEDIUM-PRESSURE LIQUID EXTRACTION OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS FROM SOIL

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A new concept for extraction of contaminated soils is described. The idea is to modify a given soil by grinding it with silica gel to destroy the interaction between the humic matter and the contaminant. Comparison of classic soxhlet extraction and soxhlet extraction of the modified soil showed similar results. The produced homogeneous phase can be used as a stationary phase of a medium-pressure liquid chromatography system. The extraction of five selected PAHs from spiked soils using the medium-pressure liquid extraction method showed excellent recoveries. The elution profiles of the substances using solvent mixtures of increasing polarity showed that the optimal eluent is a cyclohexane/acetone (9:1) mixture. This makes it likely, that a separation from halogenated aromatics can be achieved.

**KEY WORDS:** Medium-pressure liquid extraction (MPLE), PAHs, soil, extraction.

## INTRODUCTION

Interlaboratory comparison of methods used for analyzing polycyclic aromatic hydrocarbons (PAHs) in soil samples has shown that the results differ strongly<sup>1</sup>. The main cause probably is not the analytical method used: for the determination of soil contamination in general the results obtained depend mainly on the methods used for extraction. Several attempts have been undertaken to optimize these procedures<sup>2-5</sup>. We proposed a new concept for extraction of contaminated soil by means of medium-pressure-liquid-extraction (MPLE)<sup>6</sup>. The fundamental idea was to modify a given soil by grinding it with silica gel or aluminum oxide, to destroy enduringly the interaction between the humic matter and the contaminant<sup>7</sup>. The produced homogeneous powder could then be used as a stationary phase of a medium-pressure liquid chromatography system. Following the basic concept of MPLE, the contaminants were subsequently eluted from the soil by suitable eluents.

As we have shown recently, different pollutants can be eluted from these matrices by solvents of different polarity<sup>8,9</sup>. We now report about the optimization of the recovery of five PAHs from contaminated soil by this method. Due to our small budget we were only able to buy acenaphthene, phenanthrene, pyrene, chrysene and benzo(a)pyrene. We selected them from the 16 EPA PAHs more or less arbitrarily on the basis of their number of condensed rings and their molecular shape. The recovery of these contaminants from silica gel ground soil are reported and compared to those of the 'classical' soxhlet extraction. Elution profiles are discussed in view of separation of the PAHs from polychlorinated biphenyls (PCBs).

## EXPERIMENTAL

The standardized soils used for the experiments were bought from Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUF) Speyer: SP 2.1, sandy soil, Charge No. 14292; organic matter,  $0.7 \pm 0.07\%$ , particles  $< 0.02$  mm,  $7.9 \pm 1.4\%$ , and SP 2.2, sandy loam, Charge No. 24292; organic matter,  $2.29 \pm 0.37\%$ ; particles  $< 0.02$  mm,  $10.1 \pm 19.6\%$ . The soils were stored in a refrigerator at  $4^\circ\text{C}$ . The water content of the soils was controlled repeatedly by drying and weighing and showed a mean value of  $1 \pm 0.2\%$  of the dry substance for the sandy soil 2.1, and  $11 \pm 0.4\%$  for the sandy loam 2.2. Cyclohexane and acetone (zur Synthese for the extractions, Uvasol for the volumetric solutions), dimethylformamide (zur Rückstandsanalyse), silica gel 60 ( $< 63$   $\mu\text{m}$ ), silica gel Lichroprep SI 60 (25–40  $\mu\text{m}$ ) and sodium sulphate (reinst) were bought from Merck and used without further purification.

Solutions of acenaphthene, phenanthrene (Merck), pyrene (Koch-Light Laboratories), chrysene and benzo(a)pyrene (Aldrich) in cyclohexane with concentrations of 500 mg/l were prepared. These were distributed onto the native soil by the method presented below to get an even contamination of about 15 mg/kg.

500 g of sterilized standardized soil were spiked in an ISO-glass bottle by distributing 3 ml of each standard solution onto it, followed by 12 h shaking in a shaking machine. The contaminated soil was stored in a refrigerator and for each experiment aliquots of 15 g were taken. A 700 ml ceramic ball mill container and twenty ceramic balls of 20 mm diameter (Königliche Porzellan Manufaktur Berlin) were used to grind the spiked soil with 15 g of silica gel in the ball mill for 5 min to give a homogeneous powder. These 30 g of denatured soil were filled into a Büchi MPLC column (23/1.5 cm) onto 2 g of silica gel (Lichroprep) and were treated as when dry-filling a stationary phase<sup>10</sup>. Using fractions (up to 12) of 150 ml, the contaminants were extracted by different solvents at a flow rate of 12 ml/min. No pressure build-up was observed.

The eluates were cleaned up using the dimethylformamide method of VDI-Richtlinie 3873. After concentrating to about 2 ml, the fractions were diluted with 50 ml of cyclohexane and the resulting solution was extracted with 50 ml of dimethylformamide/water (9:1). The dimethylformamide phase was separated, 50 ml of water were added and the PAHs were re-extracted into 100 ml of cyclohexane. The cyclohexane phase was separated, washed twice with 10 ml water and dried with 2 g of sodium sulphate. The resulting solution was concentrated to about 1 ml under reduced pressure and then transferred into a 2 ml volumetric flask<sup>11</sup>.

The amount of PAHs was likewise determined by classical and modified soxhlet extraction. Therefore 50 g of spiked or natively contaminated soil were mixed with an aliquot of sodium sulphate or 100 g of the ground soil/silica gel mixture were placed in a soxhlet tube. The probes were extracted for 4 h with 250 ml of boiling toluene. The solvent was evaporated until a few milliliters of residue remained and these were diluted with 50 ml cyclohexane. The resulting solutions were treated like the MPLE extracts.

Quantification was done by means of calibration curves. The contaminants were determined using a Hewlett Packard 5890 II gas chromatograph with a 50 m HP1 0.32 mm ID capillary column, a split/splitless injector and a flame ionisation detector (FID). Helium was used as carrier gas and nitrogen as make-up gas. The injector and detector temperatures were  $300^\circ\text{C}$  and the temperature programme of the oven started at  $120^\circ\text{C}$  for 2 min, with a subsequent increase to  $260^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  and, after 12 min at  $260^\circ\text{C}$ , at  $40^\circ\text{C}/\text{min}$  to the final temperature of  $300^\circ\text{C}$  that was kept for 2 min.

## RESULTS AND DISCUSSION

Standard soxhlet extraction of the unspiked soils showed their native contamination. The amount of acenaphthene in soil 2.2 was too small to be quantified. The Table 1 summarizes the results.

Before determining the recoveries of the selected PAHs using MPLE, we evaluated the extraction behaviour of the ground soils under the conditions of soxhlet extraction. The fundamental idea of modifying a given soil by grinding it with silica gel was to destroy enduringly the interaction between the humic matter and the contaminants. This should work with a soxhlet extraction as well as under the conditions of MPLE. Experiments with spiked soil 2.1 showed that the recoveries obtained with silica gel ground soil were higher, but not significantly higher (Table 2).

Next, using the same spiked soil, the MPLE procedure recoveries were determined. They were found to be equal or higher than those of soxhlet extraction, if the proper eluent was used. With the non-polar solvent cyclohexane average recoveries were over 90%. This could even be improved by using cyclohexane/acetone (9:1). The PAHs were then nearly quantitatively recovered from the soil. Increasing the amount of acetone to 20 or 30%, however, significantly decreased the extraction yield of all analytes. Probably the dissolution of soil moisture and/or polar organic matter in the more polar solvent mixtures diminishes the solubility of the rather non-polar hydrocarbons. Alternatively, the PAHs are perhaps enclosed in hydrophobic cavities in the humic matter. The finding of an optimal polarity of the eluent is in agreement with similar results published for supercritical fluid extraction (SFE) of e.g. chlorobenzenes from soil<sup>12,13</sup>. For this extraction method the effect of the matrix on the extraction was recently discussed<sup>14</sup>. The optimized solvent mixture cyclohexane/acetone (9:1) was also used for soil 2.2 and

**Table 1** Native contamination of the probe PAHs ( $\mu\text{g}/\text{kg}$  dry substance) in the used soils found by standard soxhlet extraction of the non-spiked matrices;  $n = 5$ .

Soil	Acenaphthene	Phenanthrene	Pyrene	Chrysene	Benzo(a)pyrene
2.1	$63 \pm 5$	$109 \pm 5$	$175 \pm 5$	$54 \pm 3$	$131 \pm 5$
2.2	–	$64 \pm 9$	$115 \pm 11$	$72 \pm 10$	$173 \pm 9$

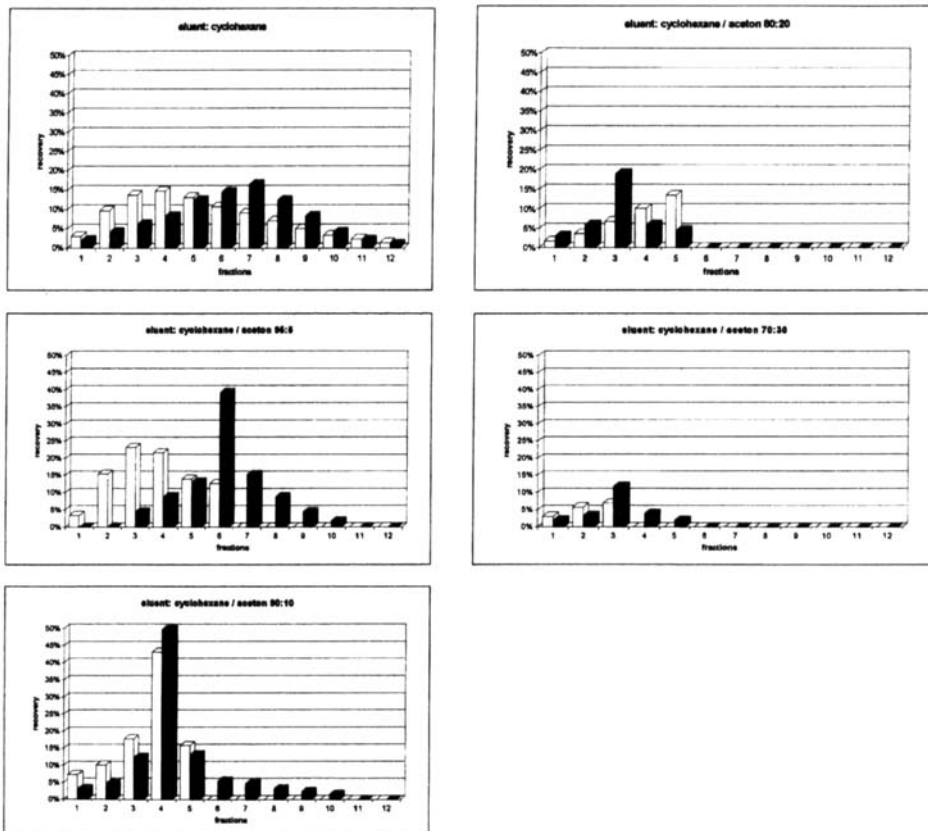
**Table 2** Recoveries (%) of the PAHs from spiked soil 2.1 by classical soxhlet extraction (soxh./sulph) and soxhlet extraction of silica gel ground soil (soxh./silica) ( $n = 5$ ) and by MPLE using solvent mixtures of increasing polarity (percent acetone in cyclohexane) ( $n = 11$  for 0 or 10,  $n = 3$  for 20 or 30) and by MPLE from soil 2.2 using cyclohexane/acetone (9:1) ( $n = 2$ ).

Soil	Method	Acenaphthene	Phenanthrene	Pyrene	Chrysene	Benzo(a)pyrene
2.1	soxh./sulph	$83 \pm 7\%$	$89 \pm 2\%$	$92 \pm 3\%$	$86 \pm 6\%$	$80 \pm 4\%$
2.1	soxh./silica	$95 \pm 5\%$	$94 \pm 5\%$	$91 \pm 8\%$	$89 \pm 7\%$	$86 \pm 8\%$
2.1	MPLE(0)	$94 \pm 3\%$	$92 \pm 4\%$	$93 \pm 4\%$	$93 \pm 3\%$	$91 \pm 4\%$
2.1	MPLE(10)	$99 \pm 3\%$	$99 \pm 2\%$	$100 \pm 2\%$	$99 \pm 2\%$	$100 \pm 2\%$
2.1	MPLE(20)	$84 \pm 9\%$	$81 \pm 3\%$	$82 \pm 8\%$	$83 \pm 5\%$	$85 \pm 4\%$
2.1	MPLE(30)	$66 \pm 7\%$	$71 \pm 3\%$	$72 \pm 5\%$	$40 \pm 4\%$	$57 \pm 4\%$
2.2	MPLE(10)	$97 \pm 0.5\%$	$97 \pm 2\%$	$101 \pm 2\%$	$98 \pm 1\%$	$101 \pm 1\%$

showed equally good recoveries. Table 2 summarizes the results obtained from the five PAHs by the different extraction methods.

As a further illustration of the process, elution profiles for two PAHs are shown in Figure 1. Increasing polarity generally causes an earlier and a sharper elution profile, but for the more polar solvents at the expense of the overall amount.

A main goal of MPLE is the successive elution of different contaminants from the modified soil. We have shown recently that hexachlorobenzene (HCB) and pyrene can be separated by this method by using cyclohexane as eluent. HCB elutes first as a sharp peak and then pyrene with the elution profile shown in Figure 1<sup>8</sup>. In general halogenated aromatic hydrocarbons like HCB or polychlorinated biphenyls (PCBs), will be extracted by the pure aliphatic solvent rather than by the more polar solvent mixtures<sup>9</sup>. Optimization of the composition of the eluents should improve the separation such that halogenated aromatics are eluted first with cyclohexane and next, the PAHs with cyclohexane/acetone (9:1).



**Figure 1** Elution profiles of pyrene (□) and benzo-a-pyrene (■) from modified soil 2.1 by cyclohexane/acetone mixtures of increasing polarity; fraction size, 150 ml.

## CONCLUSIONS

The recoveries of selected PAHs from spiked soils using the MPLE method are at least as good as those obtained using common soxhlet extraction. The elution profiles of the substances observed when using cyclohexane/acetone (9:1) suggest that a separate extraction from halogenated aromatic hydrocarbons, which can easily be extracted with pure cyclohexane, may be possible. Current studies also deal with the extraction behaviour of halogenated aliphatics such as lindane and dieldrin, and more polar pesticides from the triazine and phenol groups<sup>15</sup>.

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