Separation of Pyrene and Hexachlorobenzene by Middle Pressure Liquid Extraction (MPLE) of Soil.

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1. Introduction

The characteristics of organic chemicals in soil make clear that a concerted and reproducible recording of several different contaminants in turn is difficult [1]. As a matter of fact, no such method currently exists. Today's treatments, like extraction by shaking with suitable solvents or solvent mixtures, treatment with ultrasound or soxhlet-extraction, are best for special substances but no consecutive extraction of different contaminants can be done by them [2,3]. This is aggravated by the fact that sometimes the results obtained by using a certain method cannot be reproduced by other laboratories, and that often the results from using different methods are not comparable to each other anyway [4].

A standardizable soil treatment which will give reproducible extracts of most of the possible contaminants in succession would facilitate assessment of soils, especially for regulators.

Similar to the Supercritical-Fluid-Extraction which could be successfully performed for the PAHs and partly for the PCBs [5,6], we try to develop a soil extraction method using a Middel-Pressure-Liquid-Chromatography system as an extraction unit [7]. Most important idea was to ground the soil with an inert salt and by this create a denatured soil. This plays the role of the stationary phase of the system and solvents or solvent mixtures of different polarity elute the different organic chemicals. The treatment of a standard soil shows that the PAH Pyrene and the halogenated hydrocarbon Hexachlorobenzene (HCB) could be extracted well.

2. Experimental

We spiked 100 g of standard soil (LUFA Speyer Charge No. 14292) in an ISO-glasbottle by distributing 100 µl each of the Pyrene (Koch-Light-Laboratories) solution (0.5 g/l) and the HCB (Fluka) solution (0.5 g/l) in cyclohexane onto it followed by 3 h shaking in a shaking machine. The spiked soil was ground with 100g of either sodiumsulfat, aluminium oxid or silica gel in a ball mill for half an hour to result a homogenous powder. This denatured soil was given onto 30 g of silica gel which were filled in the column of a Büchi Middel Pressure Liquid Chromatographic system and was treated like dry-filling of a stationary phase [8]. Cutting fractions of 10 ml the contaminants were extracted by different solvents at a flow rate of 2 ml/min and the pressure between 3 and 5 bar (Figure 1). Pyrene was determined using a Perkin-Elmer fluorescence spectrophotometer MPF-3L, Hexachlorobenzene by the Perkin-Elmer UV-Vis spectrophotometer 550.

3. Results and Discussion

Using toluene or xylene as mobile phase, nearly quantitative recovery rates could be found for Pyrene and HCB independent of the inert salt applied. However, both contaminants elute together in the first fraction and the extracts had to be cleaned up by silica gel/ hexan similar to the soxhlet-extracts 2) before the measurements. In order to find a separation of the substances and hoping to spare the clean up we tried hexane and cyclohexane as the extracting solvent. In case of sodiumsulfate as an inert salt this led to no reproducible extraction, Pyrene and HCB elute without clear sepa-

ration in changing order. Furthermore the recovery rates were poor, up to 70 % for Pyrene but only 40 % for HCB. The results were improved by using aluminum oxide or silica gel, respectively. Although a clear separation of the two substances did not take place their elution profiles were sharp. Both eluted within the first fractions and recovery rates were up to 80 %. First experiments with Lindane and Dieldrin, respectively, showed no extraction of these aliphatic chlorocarbons under this conditions. Application of a solvent mixture cyclohexane:acetone (8:2) seems to extract them well. This work is still under study.

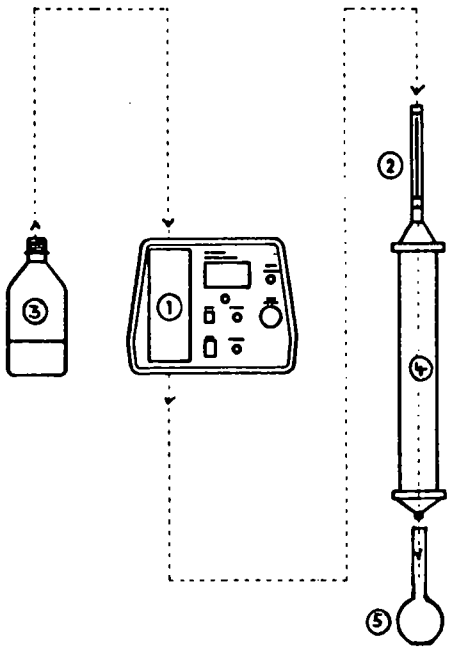

Figure 1: Modified Büchi chromatographic system for Middel Pressure Liquid Extraction (MPLE) of denatured soil; 1 pump, 2/4 column with contaminated soil, 3 solvent, 5 extract.

4. References

1) Korte F.(1980): Lehrbuch der Ökologischen Chemie, Georg Thieme Verlag Stuttgart.
2) Wahle U. (1990): Analysenschema für organische Stoffe in Böden, Dissertation Universität Duisburg, Wissenschaftsverlag Dr. W. Marein, Frankfurt a.M..
3) Wahle U., Th. Heidrich, W. Kördel (1993) : Extraktionsverfahren zur Erfassung des bioverfügbaren Schadstoffanteils in Böden, 24.GdCh-Hauptversammlung, Hamburg
4) Blankenhorn I., D. Meijer and R.J. Delft van (1992) : Interlaboratory comparison of methods used for analyzing polycyclic aromatic hydrocarbons (PAHs) in soil samples; Fresenius J.Anal.Chem. 343, 497-504.
5) Dahmen N. (1993) : Workshop on Supercritical Water and Fluid Chemistry, Nachrichten aus Chemie, laboratorium und Technik 41.
6) Wunsch A. (1993) : Über die Einsetzbarkeit der SFE mit überkritischem Kohlendioxid zur quantitativen Bestimmung von polycyclischen Biphenylen aus Bodenproben, Diplomarbeit FH Darmstadt.
7) Hüttenhain S.H., U. Wahle (1993) : Deutsches Patentamt, Offenlegungsschrift DE 4129195 A1.
8) Talamona A., E. Stump : Präparative Mitteldruck-Flüssigchromatographie Teil1, Büchi Laboratoriumstechnik Ag, Flawil/Schweiz.