Medium - Pressure - Liquid - Extraction (MPLE) of selected Chloropesticides from Soil (MPLE IV) [1)]

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Abstract

The extraction of Lindane, Heptachlor, Heptachlor-endo-epoxid, Chlordane and Dieldrin from spiked soils using the Medium-Pressure Liquid-Extraction method showed recoveries comparable to classical soxhlet extraction. Recoveries showed a significant effect on the modification of the solvent polarity so that the aspired separation from other contaminants seems likely

1 Introduction

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 [2-6)]. The reason for this is probably the enclosure of pollutants in the humic matter of the soil [7,8)]. We propose a new extraction method for contaminated soil. The initial step of sample preparation is the grinding of the respective soil with silica gel to alter the matrix. The produced homogeneous powder can be used as a stationary phase of a medium pressure liquid chromatography system. As we have shown lately, different pollutants can be eluted from this by solvents of different polarity [9-12)]. We now report the recovery of five Chloropesticides from contaminated soils by this method.

2. Experimental

A solution of Lindane (Merck), Heptachlor, Heptachlor-endo-epoxid, Chlordane and Dieldrin in cyclohexane with concentrations of 1 µg/l each was prepared. 140 µl of this solution were distributed onto 15 g of sterilized standardized soil (LUFA Speyer Sp 2.1 Charge No. 14292, sandy soil) in an ISO-glass bottle, followed by 12 hrs shaking in a shaking machine. After adding 15 g of silica gel, the spiked soil was ground in a 500 ml Retsch ceramic ball mill container with 10 ceramic balls of 20 mm diameter (Königliche Porzellan Manufaktur Berlin) for five minutes at 500 rpm to give a homogenous 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, Merck) and was treated like dry-filling of a stationary phase [14)]. Cutting fractions of 70 ml, the contaminants were extracted by cyclohexane/acetone mixtures at a flow rate of 10-15 ml/min. The pressure varied between 2 and 4 bar. No clean up procedure was necessary after elution. The resulting solutions were concentrated to about 1 ml under reduced pressure, and then transferred into a 2 ml volumetric flask.

The contaminants were determined using a Hewlett Packard 5890 II gaschromatograph with a J&W capillary column (DB 5-60N 0,23 mm ID 0,25µm film), split/splitless injector and Electron-Capture-Detector (ECD). 1. Quantification was done via calibration curves.

3 Results and discussion

Standard soxhlet extraction with toluene followed by silica gel clean-up of the unspiked soils showed their native contamination[15]. Only 3.0 ± 0.3 µg/kg Lindane and 2,5 ± 0.1 µg/kg Dieldrin could be doubtlessly identified. These basic contamination levels were subtracted from the extraction results of the spiked soils to calculate the recovery rates.
Likewise the extraction behavior of the spiked soils was evaluated before determining the recoveries of the selected chloropesticides using MPLE. Except for Heptachlor-endo-epoxid, which was completely lost, recoveries of the soxhlet extraction of the spiked soils were good (Table 1). Next the MPLE procedure recoveries were determined. As a dependency of the extraction rates on the solvent polarity of the eluent had already been proofed, two different solvent mixtures were used: cyclohexane/acetone 90:10 and 65:35. Recoveries were found to be more or less equal to those of soxhlet extraction, if the proper eluent was used, but not significantly higher. Table 1 summarizes these results.

Method	Lindane	Heptachlor	Heptachlor-endo-epoxid	Chlordane	Dieldrin
soxhlet	74±1	144±1	0	115±1	119±1
MPLE 10	111±1	73±8	87±1	81±1	55±2
MPLE 35	0	154±34	105±3	98±2	78±2

Table 1: Recoveries (%) of chloropesticides from spiked soil 2.1 by classical soxhlet extraction, n = 5 and by MPLE (solvent mixtures of increasing polarity; percent acetone in cyclohexane), n = 5.

Similar to Hexachlorobenzene and the polycyclic biphenyls Lindane is extracted best using a non-polar solvent. In respect to a successive elution of contaminants from a ground soil it will probably coeluted with those substances. Recoveries of the other pesticides are generally better using solvent mixtures of higher polarity, but recoveries using the cyclohexane/aceton 9:1 mixture are at least sufficient with the exception of Dieldrin, which eluted poor under the non-polar conditions.
But unlike polycyclic aromatic hydrocarbons, the elution of the selected aliphatic chlorohydrocarbons showed no significant effect on the modification of the solvent polarity by adding different amounts of acetone. The basic concept of the MPLE is the successive elution of different groups of contaminant from soil using eluents of different polarity. Under conditions of cyclohexane/aceton 9:1, the possibly present PAHs would be extracted as well. Further experiments - especially on the nature of the grinding material applied - must be conducted on the modification of the soils. Different solvents and solvent mixtures are still under study to elute successively PAHs, PCBs and chloropesticides from those soils. However, the most hopeful experiments presently are the use of a heated extractioncolumn and a second column filled with silver nitrate coated silica gel for the separation of the contaminants.

4. References

1) From J. Feick, Entwicklung einer Extraktionsmethode für aliphatische Organochlor-Verbindungen aus Boden mittels Mitteldruckflüssigkeitschromatographie (MPLE)
Diploma-Thesis, Fachhochschule Darmstadt, 1995.
2) U. Wahle, Analysenschema für organische Stoffe in Böden, Wissenschaftsverlag Dr. W. Marein, Frankfurt a.M.,
Dissertation Universität Duisburg 1990.
3) U. Wahle., Th. Heidrich, W. Kördel: Extraktionsverfahren zur Erfassung des bioverfügbaren Schadstoffanteils in Böden,
24.GdCh-Hauptversammlung, Hamburg (1993).
4) A. Wunsch, Über die Einsetzbarkeit der SFE mit überkritischem Kohlendioxid zur quantitativen Bestimmung von polychlorierten Biphenylen aus Bodenproben,
Diploma-Thesis, FH Darmstadt, FbC 1993.
5) I. Blankenhorn., D. Meijer and R. J. van Delft, Interlaboratory comparison of methods used for analyzing polycyclic aromatic hydrocarbons (PAHs) in soil samples;
Fresenius J.Anal.Chem. 343, 497, (1992).
6) U. Hechler, J. Fischer, S. Plagemann, Comparison of different extraction methods for the determination of polycyclic aromatic hydrocarbons in soil,
Fresenius J. Anal. Chem., 351, 591, (1995).
7) V. Seidel, W. Lindner, Evaluation of a Supercritical Fluid Extraction method for Hexachlorobenzene from artificially spiked and naturally contaminnated oil seeds and soil samples,
Inter. J. Environ. Anal. Chem. 59, 1, (1995).
8) H.-R. Schulten, The three-dimensional structure of humic substances and soil organic matter studied by computational analytical chemistry,
Fresenius J.Anal.Chem. 351, 62, (1995).
9) A. A. Clifford, M. D. Burford, S. B. Hawthorn, J. J. Langenfeld, D. J. Miller; Effect of Matrix on the Kinetics of Dynamic Supercriticasl Fluid Extraction,
J. Chem. Soc. Faraday Trans., 91(9), 1333, (1995).
10) S. H. Hüttenhain, U. Wahle, Verfahren zur Bestimmung von Verunreinigungen kontaminierter Bodenproben, Deutsches Patentamt,
Offenlegungsschrift DE 4129195 A1 (1993).
11) S. H. Hüttenhain, C. Wilhelm, C. Holley, J. Windrich, J. Arnold, M. Kampe, Separation of Pyrene and Hexachlorobenzene by Medium Pressure Liquid Extraction (MPLE) of Soil, Chemosphere 31, (1995), 2747
12) S. H. Hüttenhain, J. Arnold, Medium-pressure Liquid Extraction (MPLE) of selected Polychlorinated Biphenyls from soil (MPLE II), Toxicol. Environm. Chem.,in press
13) S. H. Hüttenhain, J. Windrich, Medium-pressure Liquid Extraction of selected Polycyclic Aromatic Hydrocarbons from soil, Inter. J. Environm. Anal. Chem., in press
14) Talamona A., E. Stump Präparative Mitteldruck-Flüssigchromatographie Teil1, Büchi Laboratoriumstechnik Ag, Flawil/Schweiz.
15) W. Specht, M.Tillkes, Gaschromatographische Bestimmung von Rückständen an Pflanzenbehandlungsmitteln nach Clean-up über Gelchromatographie und Mini-Kieselgel-Säulenchromatographie. Fresenius J.Anal.Chem. 301, 300-307, (1980).