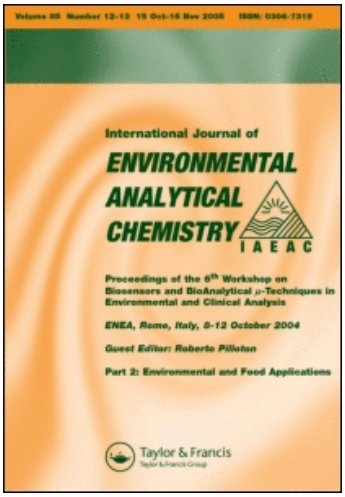

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MICROWAVE ASSISTED SOLVENT EXTRACTION (MASE) OF ORGANOCHLORINE PESTICIDES FROM SOIL SAMPLES

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The use of Microwave Assisted Solvent Extraction (MASE) for the liquid-solid extraction of a group of organochlorine pesticides from soil samples was investigated. Analysis of the pesticides took place by gas chromatography with electron-capture detection. To optimize MASE, several extraction solvents and solvent mixtures were tested. Also the influence on the extraction of the amount of water added to the soil samples before MASE was studied.

The developed procedure was applied to the extraction of a group of 16 organochlorine pesticides and metabolites from different soil types (clay, sand, peat and upper layer). The same samples were extracted by a conventional liquid extraction method. Comparing the obtained results indicated that MASE yields recoveries that are equal to or better than obtained by the conventional method, e.g 90–100% vs. 45–102% with RSDs in the range 2–6% vs. 4–22%, respectively. The developed MASE procedure also considerably reduces organic solvent consumption, extraction time and the amount of manual operation.

The selectivity of MASE was highly dependent on soil composition. For samples with a high organic content, a simple SPE clean up procedure over silica is required before analysis. The sensitivity of the method is at the sub ppb level in soil for all the compounds analysed (ppb level for upper layer). The developed MASE procedure was applied to the analysis of 120 soil samples with possibly incurred residues.

Keywords: MASE; organochlorine pesticides; soil; analysis

INTRODUCTION

During the last decade, many papers concerning the solvent extraction of organic compounds by using microwave radiation have been published.[1–12] Although Microwave Accelerated Solvent Extraction (MASE) is a rather new technique,

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its applicability is already considerably wide, ranging from the extraction of DNA from paraffin-embedded tissue[1] to the extraction of aromas from wine.[2] However, the majority of the recently published applications deals with the extraction of pesticides and organic contaminants from environmental samples, especially soils and sediments. Polynuclear aromatic hydrocarbons,[3] organochlorine and organophosphorous pesticides,[4,5] petroleum hydrocarbons[6] and triazines[7,8] have been extracted by MASE. All these papers clearly show the advantages of MASE with respect to the extraction efficiency and operating time when compared with conventional techniques like liquid extraction or even with respect to modern techniques like Supercritical Fluid Extraction (SFE).[9] In general, MASE reduces extraction time, solvent consumption and time of manual operation, and increases both extraction efficiency and reproducibility. The selectivity however, seems not to be strongly considered in the literature.

In previous papers[8,10,11] we showed the applicability of MASE for the extraction of triazines from soils. Based on an experimental design, in which a number of MASE parameters was studied, it was shown that the extraction is mainly dependent on the temperature, extraction time, sample matrix and extraction solvent. These parameters are effecting extraction efficiency and/or selectivity. In order to provide efficient extraction of the desired analytes and minimal co-extraction of matrix interferences, the selection of an appropriate extraction solvent is a crucial point in the procedure. The use of nonpolar solvents will be preferable, as they reduce the co-extraction effect and are compatible with instrumental analytical (GC) techniques used for a large number of pesticides. However, according to the principles of microwave energy transfer nonpolar solvents (n-hexane, cyclohexane or petroleum ether) are not the most suitable solvents for microwave extraction, as they are very poor absorbing media. Moreover, the accessability of adsorbed compounds to be extracted from soil with a non-polar solvent is also poor.

This paper deals with the extraction and determination of a group organochlorine pesticides (OCPs) in soil samples, paying special attention to the selectivity of the extraction step. The dependence of the selectivity on the nature of the extraction solvent and the sample matrix have been studied. To overcome the disadvantage of using n-hexane, 20% of water was added to the samples together with n-hexane in order to transfer energy to the sample during the extraction, and to make the OCPs more accessible for their extraction.

The efficiency of the MASE procedure was similar for all studied matrices. However, the selectivity of the MASE procedure was dependent on the sample matrix. In order to increase selectivity, soils with a high organic content required an additional clean-up step over silica SPE. Both extraction parameters, efficiency and selectivity, have been compared with a conventional liquid extraction

procedure. The results obtained have permitted to develop a MASE extraction procedure for OCPs which has been applied succesfully for their analysis in soil samples with incurred residues.

EXPERIMENTAL

Reagents

All OCPs were obtained from Promochem (purity >99%, Dr. S. Ehrenstorfer, Wesel, FRG). All stock solutions and further dilutions were prepared in n-hexane (Promochem) for using as standard, and in acetone for spiking purposes, respectively. n-Hexane and acetone were from Baker (Deventer, The Netherlands). Sodium sulphate (anhydrous) was from Merck (Darmstadt, FRG).

Equipment

A MES-1000, 950-W laboratory Microwave Extraction System (CEM Corp., Mathews, NC) configured with a 12-position carousel. This extractor is capable of both temperature- and pressure-controlled operation in open and sealed vessels. The instrument controlled either pressure or temperature, depending on which parameter reached its control set point first. Teflon lined extraction vessels with a volume of 100 ml were used.

The dual column GC-ECD system consisted of a 3500 Capillary Gas Chromatograph equipped with a Model 8200 Autosampler both from Varian (Walnut Creek, Ca). The GC separation was simultaneously performed on a 25 m × 0.32 mm I.D. HP-01 capillary column with a film thickness of 0.17 μm, and on a 30 m × 0.32 mm I.D. HP-17 capillary column with a film thickness of 0.15 μm, both obtained from Hewlett Packard (Avondale, PA, USA). The oven temperature was programmed as follows: 80°C (2 min), 150°C(30°C/min), 175°C(4°C/min), 220°C(2°C/min), 275°C (15°C/min) and 3 min hold at 275°C. Helium was used as carrier gas at a flow of 2 ml/min. and as make-up gas at a volumetric flow rate of 22 ml/min. The injection volume was 4.0 μl (2.0 μl for each column), the injector temperature 220°C, and the detector temperature 300°C.

Confirmation analyses were conducted on a GC-MS system consisting of a Hewlett-Packard GC, equipped with an Autoinjector A2000S split-splitless injector from Carlo Erba, coupled to a Finnigan-MAT SSQ710 operating in the positive chemical ionisation mode. Helium was the carrier gas at a constant flow of 1.5 ml/min., and methane was the reagent gas at a pressure of 1936 mT. A

30 m × 0.25 mm i.d. (0.25 μm film) HP-01 (Hewlett Packard) was programmed from hold 1 min. at 70°C, and from there to 130°C at 30°C/min, 10°C/min to 220°C, 15°C/min to 280°C, and hold 15 min at this temperature. Spitless injection (split open 0.75 min.) was performed at an injection temperature of 230°C. Other MS parameters were source temperature 150°C, electron energy 70 eV, filament emission current 50 μA, conversion dynode voltage 1300 V.

Extraction/Clean Up Procedures

MASE

A 6.0 g portion of soil, weighed into an aluminium paper, was transferred quantitatively to the extraction vessel. Subsequently, 30 ml of extraction solvent was added to the samples and the extraction vessels were closed. Extractions were performed at 115°C for 20 min. at 100% of power and at a preset maximum pressure of 100 psi. After the extraction, the vessels were allowed to cool to room temperature before they were opened.

For MASE-experiments the following solvent mixtures were evaluated: Test 1, acetone :n-hexane (1:1;v/v); Test 2, n-hexane (samples were hydrated with 20% water); Test 3, methanol-n-hexane (10:90; v/v). For Test 1, 15 ml of solvent, corresponding to 3 g of soil, was filtered over anhydrous sodium sulphate and processed further according to the liquid extraction procedure described below (*see liquid extraction*) or concentrated to 5 ml for direct injection onto the GC-system.

For Test 2 and Test 3 a volume of organic solvent, corresponding to 3 g of soil, was dried over anhydrous sodium sulphate and collected into a calibrated tube. The solvent was concentrated to approximately 2 ml with Kuderna Danish. n-Hexane was added up to a volume of 5 ml. An aliquot was injected onto the gas chromatographic system.

Clean-up

SPE silica cartridges (100 mg) from Baker were conditioned by washing with 4 ml n-hexane, followed by transferring 1 ml of sample extract to the cartridge. Hereafter, the cartridge was eluted with 15 ml n-hexane, that was collected in a tube and subsequently evaporated to dryness on a waterbath. The residue was redissolved in 1 ml n-hexane and an aliquot was injected onto the gas chromatographic system.

TABLE I Macro parameters of the various investigated soil types.

Type of soil	*pH*	*Water content (%)*	*Organic matter content (%)*	*Organic carbon content (%)*
Test soils:				
Medium humic sand	3.9	16	1.7	0.4
Rich humic sand	5.5	9.2	5.3	1.4
Peat	5.8	6.0	30.4	16.7
Sea Clay	7.9	17.9	3.8	1.2
Collected samples:				
Upper layer forest	3.5–3.9	54–72	16–37	
Sand forest	3.5–3.9	12–26	2.4–11.2	
Sand agricultural	5.3–6.0	12–26	3.9–7.5	

Liquid Extraction

Aliquots of 25 g of soil were extracted twice with 40 ml acetone during 30 min. using a shaking machine. The organic layer was separated by centrifugation. The combined liquid fractions were mixed with 800 ml water and were then extracted twice with 50 ml hexane. The combined hexane fractions were dried over anhydrous sodium sulphate, and concentrated with Kuderna-Danish till approximately 5 ml. n-Hexane was added to the extract up to a volume of 10 ml. An aliquot was injected onto the gas chromatographic system.

RESULTS AND DISCUSION

Optimization Conditions

Based on previous experience[8,10,11] the most important parameters in optimizing MASE procedures are considered to be the temperature and pressure, and the extraction solvent. According to the findings of Lopez-Avila et al.,[4] who worked with identical MASE equipment, a temperature of 115°C and a pressure of 100 psi were selected as parameter settings. Furthermore, the instrument was operated at 100% power during 20 min. extraction time, with 12 vessels simultaneously. In Table I macro parameters for the various investigated soil types are given.

n-Hexane was selected as the principal extraction solvent because i) its excellent solubility for OCPs, ii) its non polar character reducing the extractability of interferences, and iii) its compatibility with the GC system. However, due to the fact that n-hexane is not the most appropiate microwave extraction solvent, different modifiers were added in order to favour the absorption of microwave

energy.[12] The addition of a modifier also greatly improves the accessability of the OCPs to be extracted from soil.

The presence of water in a sample seems to be another important MASE extraction parameter. Due to its physical-chemical properties it is able to absorb microwave radiation and, what is even more important, transfer the absorbed energy to the rest of the sample.[13]

With respect to soil samples, there is an ongoing discussion about the condition (wet or dried) on which the sample should be in order to perform an efficient extraction of residues. Thus the effect of the moisture content of the samples on the recoveries of OCPs was studied. The objectives were to study the general effect of water in the MASE extraction technique, and how it can effect the extraction of OCPs from soil with n-hexane. These experiments were done in peat which, due to its high organic matter content, was expected to be one of the most difficult soil types under investigation.

Different percentages of water (0–45%) added to the soil were assayed. Without the addition of water the MASE device can not work while problems of overheating are observed. The soil sample is absorbing microwave energy, this energy is converted into heat resulting in an increasing temperature of the soil. Due to the fact that heat transfer to the hexane phase is poor, hexane vapour is not easily formed. This means that the pressure in the vessel is rising slowly. When the samples were dried (0% added water), the pressure reached was about 25 psi.while the temperature measured by the probe was about 90°C. These conditions are too critical to have a good extraction.

The presence of water allows a rapid heat transfer to the hexane phase resulting in a quicker formation of hexane vapour. Thus more stable extraction conditions are established (P = 75 psi, T = 100°C).

On the other hand, a high water amount (>45%) caused instability in both pressure and temperature, resulting in less reproducible recovery values. High percentages of water probably also reduced the accesibility of the solvent to the soil. Addition of water between 10 to 25% gave an efficient extraction, as shown in Figure 1. It was concluded that it is not possible to perform a good MASE extraction for dried and very wet samples when n-hexane is used as the principal extraction solvent.

The effect of choice of extraction solvent for MASE of OCPs from soil was studied. The extractability was tested with freshly spiked sandy soil samples.

As can be seen in Table II, similar recoveries were obtained independently of the extraction mixture used (Test 1, 2 and 3). In fact, with respect to interferences, the use of MASE followed by liquid extraction [MASE (1)*] in stead of MASE alone gave a slightly better selectivity, but then a laborious clean-up procedure was required. Using n-hexane (20% water added to the sample) no

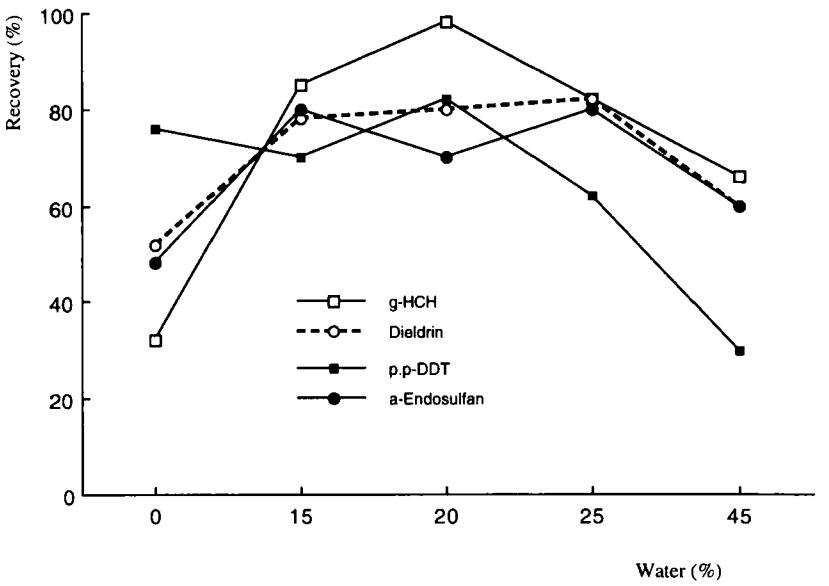


FIGURE 1 Recovery vs water % for some typical organochlorine pesticides.

solvent exchange is required, and the loss of analytes during the sample preparation can be reduced. Thus n-hexane (plus 20% water) was selected as the extraction solvent and was employed for all further experiments.

In order to validate the efficiency of the MASE procedure, the soil samples were also extracted by a conventional liquid extraction procedure derived from the procedure described by Wegman and Hofstee.[14] The results also given in

TABLE II Recoveries and RSD(%) corresponding to the extraction of OCPs from spiked sand samples (10 μg/kg), by using MASE and conventional liquid extraction procedures. MASE 1, acetone:n-hexane (1:1 ⊨ v), MASE 1*, acetone:n-hexane (1:1) followed by liquid extraction; MASE 2, n-hexane (samples were hydrated with 20% water); MASE 3, methanol-n-hexane (10:90; v/v).

OCPs	*MASE (1) (n = 3)*	*MASE (1)* (n = 3)*	*MASE (2) (n = 9)*	*MASE (3) (n = 3)*	*Conventional extraction (n = 3).*
HCB	113 ± 5	105 ± 2	98 ± 2	127 ± 0	87 ± 4
α-HCH	119 ± 3	102 ± 4	97 ± 4	109 ± 1	100 ± 4
γ-HCH	126 ± 2	105 ± 1	101 ± 3	111 ± 3	81 ± 22
β-HCH	85 ± 8	96 ± 5	96 ± 6	50 ± 4	100 ± 3
β-HEPO	94 ± 8	103 ± 3	91 ± 2	113 ± 1	101 ± 3
pp-DDE	99 ± 8	96 ± 7	88 ± 2	101 ± 7	45 ± 20
Dieldrin	92 ± 5	100 ± 3	88 ± 2	106 ± 5	93 ± 4
op-DDT	102 ± 1	101 ± 0	86 ± 2	87 ± 9	65 ± 15
pp-TDE	99 ± 8	82 ± 5	82 ± 4	83 ± 9	102 ± 6
pp-DDT	105 ± 5	109 ± 6	84 ± 6	74 ± 13	94 ± 11

Table II, confirm that higher and more reproducible recoveries can be obtained by using MASE.

With the MASE method, the sample preparation time can be reduced to less than 1 hour, and solvent consumption is less than 35 ml. In comparison, the conventional liquid extraction procedure takes several hours and uses hundreds of mililiters of organic solvents.

Soil Type

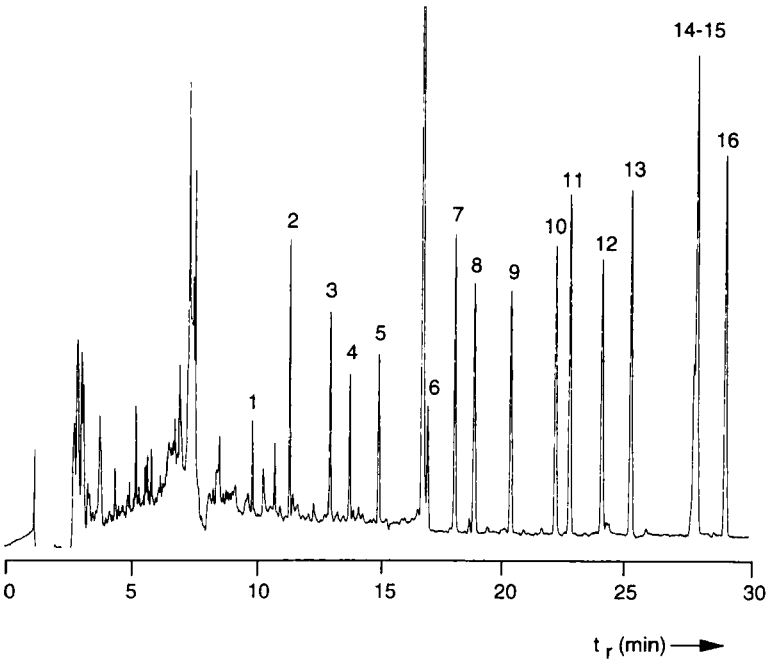
The developed MASE procedure was tested on different soil types; clay, peat, sand and top soil from the forest (upper layer). Standard test soils, blanks as well as spiked samples, were used for the optimization of the MASE procedure. Both the water and organic content of these soils are given in Table I.

Freshly spiked samples were prepared by adding an appropriate volume of spiking solution to homogenized soil samples; the samples were then air-dried overnight and were extracted the next day.

Samples with aged residues were prepared by spiking samples at a level of 10 or 100 μg/kg for each analyte. These samples were stored in a refrigerator at 4°C for almost 1 year before analysis. In Figure 2 a chromatogram of a sandy soil sample, freshly spiked at a level of 2.5 μg/kg with the compounds of interest, is shown.

In order to validate the method, freshly spiked soil, and spiked soil aged for 1 year and stored at 4°C, were extracted. In Table III the recoveries obtained from this experiment are shown. As can be seen, good recoveries were obtained for sandy soils (high organic content), peat and clay. Although these samples were stored for one year and the component-matrix interactions might be different compared to the freshly spiked samples, there were no problems in extracting the OCPs.

The extraction efficiency was independent of the soil type. The selectivity however was dependent on the soil composition. All the extracts, except from upper layer, were directly injected into the GC-ECD system, without causing any matrix problems. For upper layer, the MASE extracts were not clean enough and in order to protect the GC-system a rapid clean-up step was performed (see experimental section). Figure 3 shows the chromatograms corresponding to upper layer extracts without (3A) and with SPE clean-up (3B). Obviously, by cleaning the samples, the selectivity improves and thus also the sensitivity. A volume of 15 ml n-hexane was required to elute the selected OCPs, except β-Endosulphan, from the Si-OH cartridges. By using soil samples, some deactivation of the column was observed and 12 ml of solvent was the required elution volume. Nevertheless the reproducibility and repeatibility were good enough.



Column HP17

Peak identification: 1. HCB, 2. α-HCH , 3. γ-HCH , 4. β-heptachlorepoxide , 5. Aldrin, 6. β-HCH , 7. ∂-HCH, 8. β-Hepo, 9. α-Endosulfan, 10. p,p'-DDE, 11. Dieldrin, 12. Endrin, 13. o.p'-DDT, 14. p,p'-TDE , 15.β-Endosulfan, 16.p,p'-DDT.

FIGURE 2 GC-ECD analysis of extracts of a freshly spiked sandy soil sample (spiking level about 2.5 μg/kg) obtained after MASE using n-hexane as extraction solvent (hydration of sample 20%).

About 25 ml were required for the elution of β-Endosulphan. Adding 1% of acetone to the elution solvent (n-hexane), only 2 ml were required. The clean-up did not change the recovery values.

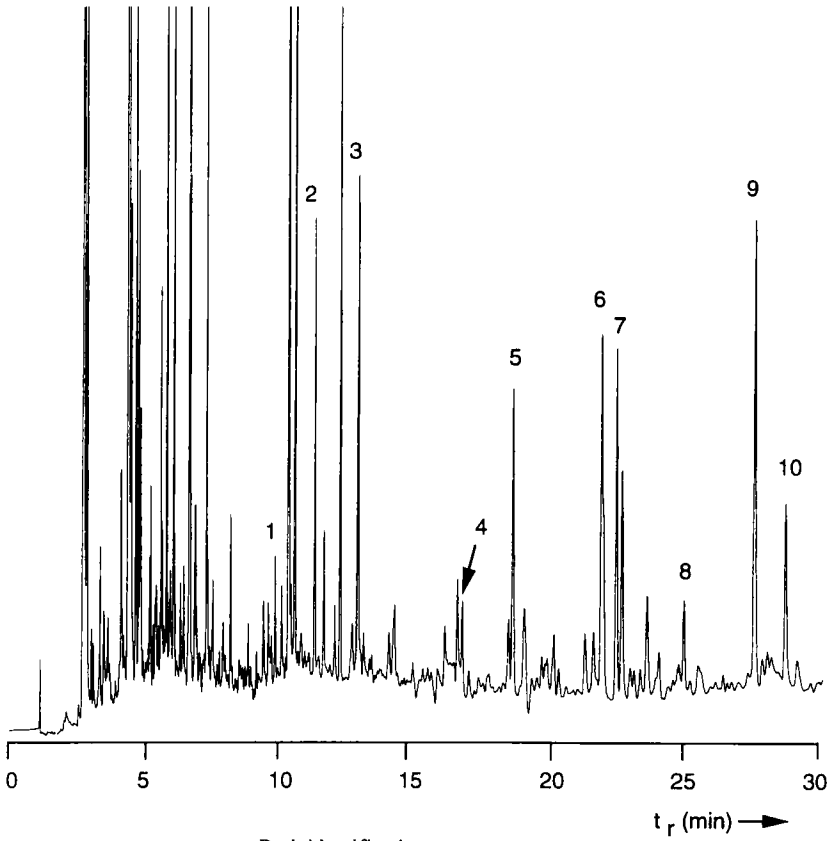
Soil Samples With Incurred Residues

One of the possible problems in the analysis of real samples using MASE, can be the heterogeneity of the samples. Taking into account that with the MES-1000 apparatus 12 samples can be extracted simultaneously but only one can be temperature and/or pressure controlled, the conditions in the different vessels can be different, depending on the consitution of the specific soil. Actually, we

TABLE III Recoveries and RSD (%) obtained for the extraction of OCPs from different soil types (freshly spiked and aged residue samples) by using the MASE procedure. Spiking level 10 μg/kg, n = 3

OCPs	***Clay***		***Peat***		***Humus Rich***	
	Fresh spiked	*Old residue*	*Fresh spiked*	*Old residue*	*Fresh spiked*	*Old residue*
HCB(1)	74 ± 7	70 ± 8	100 ± 4	85 ± 4	97 ± 2	80 ± 5
α-HCH(2)	97 ± 6	81 ± 5	103 ± 2	89 ± 3	96 ± 4	73 ± 10
γ-HCH(3)	105 ± 5	94 ± 8	82 ± 6	80 ± 2	101 ± 2	91 ± 3
HEPTA(4)	69 ± 10		92 ± 4		70 ± 2	
ALDRIN (5)	74 ± 5		80 ± 1(*)		60 ± 3	
β-HCH (6)	102 ± 6	97 ± 5	75 ± 3(*)	70 ± 4	96 ± 6	100 ± 11
δ-HCH(7)	116 ± 8		70 ± 3(*)		101 ± 3	
β-HEPO(8)	94 ± 4	80 ± 6	86 ± 1(*)	85 ± 6	91 ± 3	88 ± 4
α-ENDOSUL(9)	97 ± 1		81 ± 2(*)		98 ± 4	
pp-DDE	76 ± 7	78 ± 5	85 ± 2(*)	71 ± 3	88 ± 2	65 ± 10
DIELDRIN(11)	93 ± 7	82 ± 3	83 ± 2(*)	78 ± 4	92 ± 8	89 ± 5
ENDRIN(12)	75 ± 4		78 ± 2(*)			103 ± 6
op-DDT(13)	74 ± 10	72 ± 7	86 ± 3(*)	69 ± 7	85 ± 2	64 ± 5
pp-TDE(14)	96 ± 4	75 ± 3	84 ± 3	85 ± 3	82 ± 4	80 ± 3
β-ENDOSUL(15)	93 ± 10		52 ± 2		103 ± 5	
pp-DDT(16)	77 ± 10	65 ± 4	80 ± 5(*)	56 ± 12	84 ± 6	75 ± 6

Clay soil: recoveries corresponding to column HP01.
Peat soil: recoveries corresponding to column HP01 and HP17 (*)
Humus Rich soil = recoveries corresponding to column HP17
Fresh spiked samples contain 16 OCPs and old spiked samples 10 OCPs.

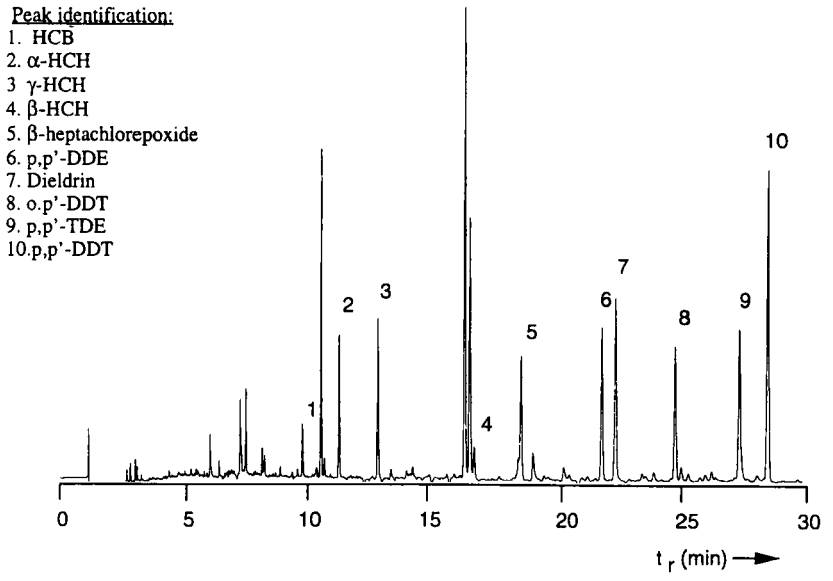


Column HP 17

Peak identification:

1. HCB
2. α-HCH
3 γ-HCH
4. β-HCH
5. β-heptachlorepoxide
6. p,p'-DDE
7. Dieldrin
8. o.p'-DDT
9. p,p'-TDE
10.p,p'-DDT

FIGURE 3 (a) Chromatogram of an upper layer sample spiked at level of 10 μg/kg. A) without SPE clean-up, B) with SPE clean-up.



Column HP 17

FIGURE 3 (b) Chromatogram of an upper layer sample spiked at level of 10 μg/kg. A) without SPE clean-up, B) with SPE clean-up.

experienced that a difference of 10–15°C in temperature inside of the vessel can be generated when 2 different samples are extracted under identical instrumental conditions. However due to the flexibility of MASE in the selection of parameter settings no differences in recoveries were observed.

As part of a monitoring program for persistent organochlorine pesticides in Dutch soils, 80 sand, 20 mineral and 20 upper layer samples collected from different sites in The Netherlands were analysed (see Table I). All the samples were extracted by MASE and in order to control the extraction at least two recoveries, at the 0.25 μg/kg and 2.5 μg/kg level, and one blank were included in each extraction run. In Table IV the recovery values are given for samples spiked on three different concentration levels. The limit of determination for each component was 0.5 μg/kg for soil (s/n = 10), and 2 μg/kg for upper layer, respectively. The data given in Table IV indicate that with regard to the S/N ratio detection at lower concentration levels is feasible. Nevertheless 0.5 μg/kg and 2 μg/kg were established as the level of determination in order to adequately

TABLE IV OCP (16 compounds) recoveries from blank sandy soil spiked at different levels (n = 3, each level) obtained after MASE and injection onto GC-ECD.

OCPs	*Recoveries and RSD(%)*		
	Level 1	*Level 2*	*Level 3*
HCB*	83 ± 11	98 ± 4	116 ± 4
α-HCH*	96 ± 2	88 ± 3	84 ± 5
γ-HCH*	95 ± 3	104 ± 7	107 ± 5
Hepta*	96 ± 4	92 ± 5	81 ± 7
Aldrin*	81 ± 2	68 ± 4	69 ± 7
β-HCH*	86 ± 5	99 ± 7	96 ± 8
δ-HCH*	92 ± 4	100 ± 6	100 ± 8
β-Hepo	93 ± 4	93 ± 6	88 ± 6
α-Endosulphan	92 ± 3	88 ± 9	79 ± 5
pp-DDE	93 ± 3	84 ± 10	98 ± 3
Dieldrin	94 ± 5	97 ± 8	91 ± 3
Endrin	96 ± 4	98 ± 10	93 ± 7
op-DDT	97 ± 6	100 ± 8	96 ± 3
pp-TDE	90 ± 5	87 ± 7	82 ± 2
β-Endosulphan	93 ± 5	101 ± 9	96 ± 5
pp-DDT	101 ± 9	94 ± 5	86 ± 1

Level 1. Concentrations between 1.1 μg/g to 10.3 μg/kg
Level 2. Concentrations between 0.5 μg/g to 4.99 μg/kg
Level 3. concentrations between 0.11 μg/g to 1.03 μg/kg
(*) Compounds quantified on the HP17 column. The other compounds were quantified on the HP01 column.

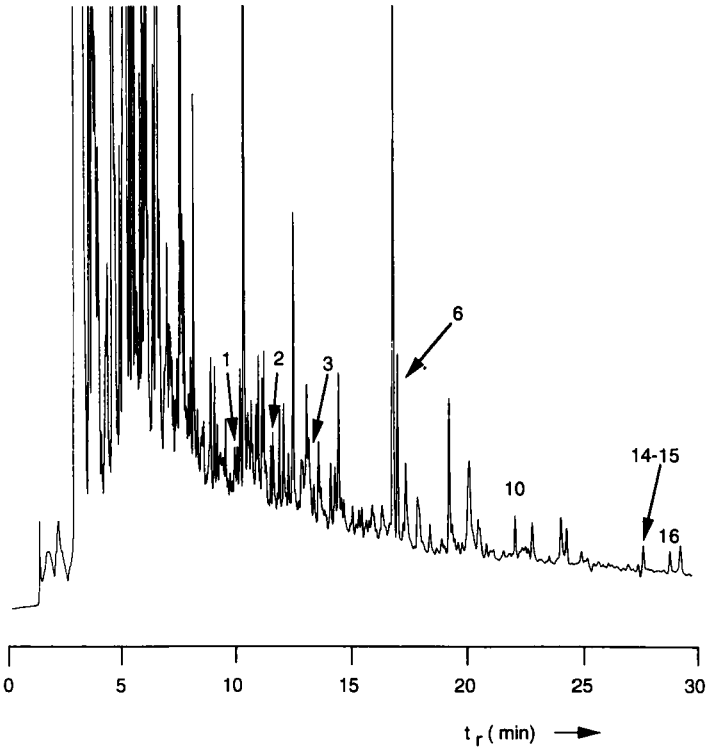
comply with confirmation analysis. Figure 4 shows the chromatogram of a sandy soil sample with incurred residue obtained on the HP-17 GC-column.

In order to confirm the results two different GC columns were used. Most of the analytes could be determined on both columns but others, because of interfering matrix peaks, could only be determined on one of the columns. Aldrin and δ-HCH could only be quantified on the HP-17 column, β-Hepo had to be quantified on the HP-01 column. The positive samples on both columns were confirmed by GC-MS.

The n-hexane extracts of the 120 soil samples (20 upper layer extracts cleaned with SPE) were directly injected into the GC-system without generating any problems in the column or in the detector. The reproducibility was good during the entire 4 weeks period of analysis, for most compounds $<6\%$, for 3 compounds 6–11%.

CONCLUSIONS

This paper shows an application of MASE for extraction of pesticides from soil samples. Using MASE conditions established in the literature, an improved extraction method for OCPs from soil has been developed. The main point has



Column HP17 Peak identification: 1. HCB, 2. α-HCH , 3. γ-HCH , 4. β-heptachlorepoxide , 5. Aldrin, 6. β-HCH , 7. ∂-HCH, 8. β-Hepo, 9. α-Endosulfan, 10. p,p'-DDE, 11. Dieldrin, 12. Endrin, 13. o.p'-DDT, 14. p,p'-TDE , 15.β-Endosulfan, 16.p,p'-DDT.

FIGURE 4 Chromatogram of a sandy soil sample with incurred residue (around the 1 μg/kg level) on the HP 17 GC column.

been centred in the optimization of selectivity, which is one of the most important parameters to be controlled. In order to increase selectivity without decreasing sensitivity, n-hexane was selected as principal extraction solvent. With established optimal conditions, different soil types, with freshly spiked and aged residues respectively, have been extracted. The obtained results show that the same conditions can be used for both, no stronger extraction conditions are required for aged residues. Moreover, no big differences in recoveries have been obtained for the different soil types. The same MASE conditions are applicable for all the soils studied. As in other publications in the literature, the high extraction efficiency of MASE is manifested. However, the selectivity of the procedure is variable, e.g. dependent on the soil type. A high organic content of the soil will result in a loss of selectivity.

Although direct injection of the soil extracts onto GC-ECD is feasible, a rapid clean-up procedure should be performed for dirty extracts, as obtained from top soil samples. For other soil types like peat, sand or clay, no additional clean-up is required.

The results obtained show that MASE is an efficient technique, that reduces extraction time, solvent comsuption and permits to obtain better recoveries in comparison to conventional techniques (liquid extraction). However, one of the possible disadvantages can be the lack of selectivity, which however can be improved by choosing the right extraction solvent and/or by including a rapid clean-up step over SPE cartridges in the procedure.

The final MASE method has been applied for the extraction of 120 samples with incurred OCP residues.

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