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EXTRACTION OF PESTICIDES FROM SEDIMENTS USING A MICROWAVE TECHNIQUE

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NWRI Contribution No. 92-20

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MANAGEMENT PERSPECTIVE

This report describes the results of a study on the optimization of statistically significant parameters associated with the extraction of organochlorine pesticides from sediments. In this report, we release the data on an environmental application of a Microwave Assisted Process (MAP™) for which Environment Canada holds the patent.

The study has shown that quantitative recovery of organochlorine pesticides can be achieved using the microwave extraction protocols outlined in the report for sediment samples. By shortening the time required for the extraction this novel technique contributes to reducing the entire analysis time to less then 50% and it allows to extract more samples simultaneously.

The new technique has advantages over organic solvent-based, liquid liquid extraction techniques in terms of reducing amount of solvents and their cost and general safety in the laboratory. These time saving and safety benefits should be considered to introduce this technique to our laboratories.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le présent rapport décrit les résultats d'une étude sur l'optimisation de paramètres statistiquement significatifs associés à l'extraction de pesticides organochlorés contenus dans des sédiments. On y indique les données sur une application environnementale d'un processus assisté par micro-ondes (MAP™) et dont Environnement Canada est détenteur du brevet.

L'étude a montré que la récupération quantitative de pesticides organochlorés peut être effectuée par des protocoles d'extraction par micro-ondes figurant dans ce rapport sur les échantillons de sédiments. En réduisant le temps d'extraction, toute l'analyse est effectuée en moins de la moitié du temps qu'il fallait auparavant et elle permet l'extraction d'un plus grand nombre d'échantillons en même temps.

La nouvelle technique présente des avantages par rapport aux techniques d'extraction à base de solvants organiques, à l'extraction liquide liquide en réduisant la quantité de solvants nécessaires et leur coût et le niveau de sécurité générale dans le laboratoire. Il faut tenir compte de ces économies de temps et des avantages sur le plan de la sécurité lorsqu'il s'agit d'introduire cette technique dans nos laboratoires.

ABSTRACT

The microwave energy produced by high intensity microwave oven, was used to extract pesticides from sediment samples. This system was compared with Soxhlet, sonification and convection heat extraction techniques. Sediment moisture and type of organic matter content are critical parameters in affecting the degree of recovery. Extraction procedure using a 30 second period repeated in sequence 5 times provided generally better recovery values than did 8 hours of Soxhlet extraction.

RÉSUMÉ

L'énergie des micro-ondes produite par un four à micro-ondes haute intensité a été utilisée pour extraire des pesticides contenus dans des échantillons de sédiments. Ce système a été comparé à l'extraction Soxhlet, à la sonification et à l'extraction par convection de chaleur. La teneur en eau des sédiments et le type de matière organique sont des paramètres critiques qui influent sur le taux de récupération. Cinq extractions consécutives de 30 secondes permettaient en général une meilleure récupération qu'une extraction Soxhlet pendant 8 heures.

INTRODUCTION

The sediments are reservoirs of environmental pollutants, particularly for the organochlorine insecticides. The environmental presence of these pesticides has aroused considerable interest as evidenced by extensive monitoring activity at national and international levels (1,2).

Environmental analytical chemists are seeking continuously to improve procedures for the determination of contaminants primarily by reducing analysis time and increasing accuracy and sensitivity. Since sediments are highly variable and complex matrices, there is no standard extraction method. Recently, microwave energy has been used to achieve fast dissolution, drying, ashing and microwave digestion (3). Ganzler et al. (4,5) summarized and discussed sample preparation method for extracting biologically active compounds from lupin alkaloids and metabolites from seeds and rat feces using microwave energy. The process of microwave extraction has been patented by Environment Canada (6). Environment Canada also holds worldwide trademark rights on a Microwave Assisted Process (MAP™). In this paper, Environment Canada is releasing the first data on its environmental applications.

The use of microwave energy as a means of extracting pollutants from environmental samples has not yet been fully evaluated. The purpose of this study was to develop a rapid, reliable and sensitive sediment extraction method using a microwave oven equipped with a highly specific energy magnetron generator. This method was compared with Soxhlet extraction and various experimental conditions were tested for their effect on extraction efficiency to determine the optimum and limiting conditions for use of these electromagnetic waves in extraction processes.

EXPERIMENTAL

Standards

Analytical reference standards of the organochlorine pesticides were obtained from the U.S.-EPA, Pesticides and Industrial Chemicals Repository, Research Triangle Park, N.C., U.S.A. and Ultra Scientific, North Kingstown, R.I. U.S.A. Purities were claimed to be greater than 98%.

Stock solutions (1 mg/mL) of each pesticide were prepared in iso-octane. Working calibration solutions were prepared in iso-octane by serial dilution of a composite stock solution prepared from the individual stock solutions.

Pesticide standard mixture

Analytical grade pesticides were used. Duplicated solutions of the pesticides shown in Table 1 were made in both acetone and iso-octane, the former for sediment treatment and the latter as an analytical standard.

Preparation of Sediment Samples

The air-dried sediment samples (50.0 g oven-dried basis) in 500 mL square bottles were treated individually by pipeting onto the sediment surface 10 mL of an acetone solution of the pesticide mixture. The bottle then was rotated to mix the sediment. The sediment used was spiked with a 100 μg amount of both pesticides (endrin and heptachlor) unless stated otherwise and the sediment was aged for at least 1 month before extraction. Their concentration in the sample was 2 mg/kg.

The second standard mixture composion is given in Table I. Using this mixture a series of sediment standards were prepared containing pesticides at 50 $\mu g/kg$ per component (for the first 8 components in the mixture given in Table I).

Solvents

All solvents used were redistilled in glass. The primary extraction solvent was iso-octane; others used were n-hexane-acetone, benzene-acetone (2:1 v/v), methanol-acetic acid, methanol and n-hexane.

Extraction Procedure

The sediment samples after aging were extracted using KENMORE Microwave/Convection oven, Model 85962. It should be noted that only a commercially available explosion-proof oven must be used, if more than a couple of samples are extracted simultaneously. Approximately 1.0 g of a sample was accurately weighed into a 5 mL Reacti-Vial. Prior to extraction, the sediment samples were saturated with distilled water and 2 mL solvent was added. The sample was extracted inside the microwave oven cavity and the microwave frequency used was matched to setup a resonant pattern at 2.45 GHz frequency as is common for all home microwave ovens. The sediment sample was extracted for 30 sec using maximum power but the content of the vial was not allowed to boil. After 30 sec, the vial was immersed into an ice bath for 2 to 5 minutes. The extraction step and cooling were repeated up to 5 times. It is recommended to establish a number of repeated extractions to obtain optimal extraction for a particular type of samples.

Cleanup of Extracts and Gas Chromatographic Analyses

The extracted sediment and solvent were centrifuged for 10 minutes and solvent was filtered through Whatman No. 42 filter paper on a Buchner funnel under

partial vacuum. The filter paper and the sediment cake were rinsed three times with the extracting solvent. The combined filtrate was subjected to gas chromatographic analyses.

The gas chromatograph (Varian, Walnut Creek, CA, USA), SE-54 crosslinked WCOT column, Shimadzu C-R4A data-handling system and conditions used for gas chromatography are listed in Table II.

RESULTS AND DISCUSSION

For the application of a new extraction method, it is desirable to study the influence of specific factors on the analytical procedure. In this study, sediment moisture, microwave effects, extraction time, pesticide concentration and pesticide type were evaluated. The results together with comparative data employing conventional techniques are presented in Tables III to VIII.

The data shown in Table III indicate that iso-octane+acetonitrile (1:1) gave the highest recovery and was better than 6 hrs Soxhlet extraction used for comparison. Iso-octane was selected as the solvent of choice because it has sufficiently high boiling point and it also was the easiest solvent to work with. When a wet sediment was used, the hydrophobic solvent gave good recoveries and with binary solvents a separation of phases occurred.

Table IV presents the effects of sediment moisture on recovery. It is apparent that sediment moisture is a significant parameter for good recovery. However, a minimum water content is necessary to perform microwave extraction. The best recovery was obtained at the 15% water level which also was the sediment saturation level. Then for all following experiments, the sediment was deactivated by the addition of water to the saturation level prior to extraction.

Since microwaves have been used to affect chemical changes in various chemical solutions (2) it was desirable to determine if exposure to microwaves would have any effect on the pesticides used. Iso-octane solutions (2 mL) containing 2 μg of both endrin and dieldrin were subjected to extraction times of 10, 20, 40 and 60 sec using the microwave energy at maximum power. The recoveries were all quantitative and there was no evidence of any breakdown or alteration in the pesticides. It seems that considerably longer periods of exposure to microwaves would be required to generate any changes.

The recovery values from sediment extracted by three different methods are compared in Table V. It is evident that microwave extraction gave better recoveries than Polytron method. There was little difference between the Soxhlet and microwave extraction methods.

Since the 30 s extraction time used up to this point was arbitrarily selected, an experiment was conducted to determine the effect of extraction time on recovery. Table VI indicates that 5 cycles of 30 sec extraction at full power was adequate for quantitative recovery.

Since 100 μg had been employed in the prior experiments, it was advantageous to determine the effect of initial concentration on recovery. Results summarized in Table VII shows that recovery values were very good, indicating that concentration, at least within the narrow range used here was not a limiting factor in obtaining quantitative recovery.

The results of microwave extraction performed at optimized conditions, indicating very good recovery are presented in Table VIII. There were no indications of any degradation of these compounds.

CONCLUSION

Although the microwave extraction method was consistently the best method, the differences in recovery over the Polytron and Soxhlet methods were often small. It must be remembered that this method employs only a 30 s burst of microwave energy repeated 5-6 times, whereas the Polytron and the Soxhlet methods use much longer extraction times. A large number of samples can be processed in a short time period using this technique. The limiting factor in the number of samples that can be processed simultaneously is the capacity of the carousel holding the extraction vials.

The need for extensive cleanup could be diminished or limited by using smaller sediment samples. On numerous occasions, after microwave extraction, the sediment was re-extracted with the Soxhlet for 6 hours and the extract found to contain negligible amounts of residues, always less than 2% of the amount added to treat sediments. It is evident that the standard deviation between duplicated samples was consistently low. Soxhlet extraction is used widely for sediment extraction but it was seen that recoveries varied from one experiment to another, as did the standard deviation, both possibly due to a channelling effect in the extraction thimble.

In conclusion, it can be stated that by using microwave extraction, organochlorine pesticide residues can be extracted faster, more reliably, quantitatively and cheaper from sediments than by conventional extraction methods.

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Table I. **Organochlorine Pesticides and their Concentrations in Sediment and the Spiking Solution**

Insecticide	**Amounts (μg/kg)**	**Conc.(pg/μL)**
Hexachlorobenzene	50	2.5
α-BHC	50	2.5
Lindane	50	2.5
Aldrin	50	2.5
trans-Chlordane	50	2.5
cis-Chlordane	50	2.5
Dieldrin (HEOD)	50	2.5
p,p'-DDE	50	2.5
Endrin	100.0	5.0
o,p-DDT + DDD	250.0	12.5
p,p'-DDT	200.0	10.0
Methoxychlor (MEY)	250.0	12.5
Mirex	150.0	7.5

Table II. **GC - Operating Conditions**

Parameter	Description
Instrument	Varian Vista 6000 - ECD and Shimadzu C-R4A data system
Column	SE-54 crosslinked; 30m x 0.25 mm i.d.; 0.25 μm film thickness
Carrier gas	hydrogen; 50cm/s
Make-up gas	nitrogen 30 mL/min
Temperature Program	70 ^{0}C for 1 minute hold; to 140 ^{0}C at 15 ^{0}C/min; then to 260 ^{0}C at 4^{0}C/min
Injection	cold on-column; 1 μL
Detector temperature	350 ^{0}C

Table III. **Comparison of Solvents for Microwave Extraction of Organochlorine Pesticides from Muffled Sediment Samples** (n = 4).

Extraction Method	Solvent	Mean % Recovery and RSD	
		Endrin	Dieldrin
Soxhlet	hexane-acetone	93.0 ± 3.7	90.6 ± 4.7
Polytron	hexane-acetone	94.1 ± 6.9	90.8 ± 8.4
Microwave	isooctane (Iso)	77.4 ± 3.1	77.1 ± 3.6
Microwave	acetonitrile (AN)	89.3 ± 3.7	90.7 ± 3.9
Microwave	Iso+AN (1:1)	95.2 ± 4.9	94.2 ± 4.1
Convection heat	Iso+AN (1:1)	23.1 ± 9.2	20.8 ± 7.7

Table IV. **Effect of Moisture Level on Extraction Efficiency from Muffled Sediment Samples** (n = 4)

Extraction Method	Moisture %	Mean % Recovery and RSD	
		Endrin	Dieldrin
Microwave	0	16.4 ± 0.8	14.1 ± 1.2
Microwave	5	91.9 ± 3.2	93.7 ± 2.6
Microwave	10	94.6 ± 3.1	95.4 ± 4.2
Microwave	15	97.7 ± 6.2	95.8 ± 4.7
Microwave	20	88.8 ± 4.0	82.5 ± 3.9
Soxhlet	20	91.8 ± 5.9	90.1 ± 6.8

Table V. **Comparison of Extraction Methods and Moisture Level on Recovery from a Referenced Sediment Sample** (n = 4)

Extraction Method	State	Mean % Recovery and RSD	
		Endrin	Dieldrin
Microwave	Wet	95.7 ± 3.1	95.3 ± 3.8
	Dry	16.7 ± 0.9	15.2 ± 0.6
Soxhlet	Wet	94.8 ± 4.9	90.8 ± 2.7
	Dry	96.2 ± 2.2	96.4 ± 3.1

Table VI. **Effect of Extraction Time on Recovery of Organochlorines from Sediment Samples** (n = 4).

Extraction Time, sec	Mean % Recovery and RSD	
	Endrin	Dieldrin
15	25.9 ± 1.0	27.1 ± 0.8
30	53.3 ± 0.9	53.0 ± 1.7
45	72.4 ± 2.8	71.5 ± 3.1
60	82.2 ± 3.2	80.6 ± 3.0
120	92.4 ± 3.7	90.3 ± 0.8
180	97.9 ± 3.6	92.4 ± 3.3
210	98.1 ± 3.7	93.1 ± 4.2
240	98.0 ± 3.9	93.2 ± 3.8

Table VII. **Effect of Pesticide Concentration on Recovery from a Sediment** (n=4)

μg Added to Sediment Sample	**Mean % Recovery and Deviation from Mean**	
	Endrin	**Dieldrin**
10	96.0 ± 1.9	96.3 ± 2.1
20	94.5 ± 1.6	98.6 ± 0.6
40	96.5 ± 0.3	97.6 ± 0.7
60	96.1 ± 0.2	95.7 ± 0.2
80	96.9 ± 0.6	97.9 ± 1.6

Table VIII. **Retention Times and Extraction Recoveries of Various Pesticides from a Sediment Sample** (n = 5).

Pesticide	**t_r (min)**	**Mean % Recovery and RSD**
Hexachlorobenzene	12.60	91.7 ± 4.8
α - BHC	12.87	83.8 ± 5.0
Lindane	14.03	86.7 ± 4.9
Aldrin	19.22	93.8 ± 4.7
trans - Chlordane	22.82	89.3 ±4.8
cis - Chlordane	23.69	85.8 ± 4.5
Dieldrin	24.94	88.8 ± 4.1
p,p' - DDE	25.21	83.8 ± 4.9
Endrin	26.12	91.5 ± 4.9
p,p' - DDD	27.66	74.0 ± 3.0
o,p - DDT	27.74	81.7 ± 4.3
p,p'- DDT	29.08	81.6 ± 4.2
Methoxychlor	33.45	95.3 ± 3.9
Mirex	34.97	81.2 ± 4.0
Decachlorobiphenyl	43.20	84.0 ± 4.9

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