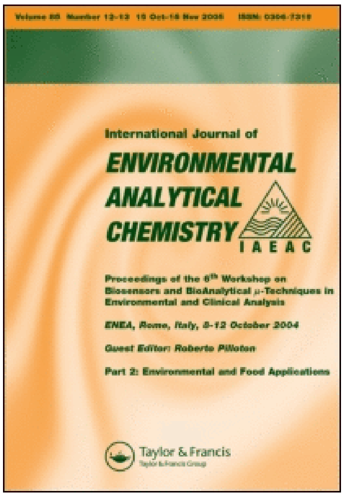

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Automated SFE Combined with GC-MS for the Determination of Organochlorine Compounds in Sludge and Sediment

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AUTOMATED SFE COMBINED WITH GC-MS FOR THE DETERMINATION OF ORGANOCHLORINE COMPOUNDS IN SLUDGE AND SEDIMENT

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Using automated supercritical fluid extraction (SFE), an analytical SFE procedure for the extraction of organochlorine compounds from sediment and sewage sludge matrices was developed and validated. The determinative step was carried out by GC-MS using selective ion recording (SIR) thus enabling high sensitivity (μg/kg level) and specificity to be achieved. The extraction method was optimised by varying selected SFE operational parameters, including extraction pressure and temperature and percentage modifier, with all results being compared to those from Soxhlet extraction.

Validation of the analytical procedure was achieved by the extraction and analysis of replicate certified reference materials, producing good reproducibility and high extraction efficiencies.

Keywords: Automated Supercritical Fluid Extraction (SFE); Sediment; Sludge; Organochlorine Pesticides (OCls); Polychlorinated Biphenyls (PCBs); GC-MS

INTRODUCTION

Analytical-scale sample preparation for the extraction of trace organic compounds from environmental matrices traditionally involved techniques such as Soxhlet and sonication extraction. Since the late 1980's analytical applications of SFE have been reported [1]. It has since grown into a competitive technique, which has proved to be an excellent alternative to Soxhlet for many analytes and matrices [2–9]. The increase in SFE development over recent years is attributed to the many advantages it has over other techniques. These include the reduction in time, labour and solvent volume, the improved or equivalent analyte recoveries, the ability to tune the extraction procedure in order to extract solutes of interest

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in a quantitative way minimising co-extraction of other matrix compounds and an increase in the overall reliability of the analytical technique [1–5, 7, 10–15].

Much research has been published on the use of SFE for the extraction of organochlorine compounds from environmental matrices [2, 8, 10, 13, 16–26]. Many of these investigations had reported contamination levels in the mg/kg range, or even used spiked matrices [2, 13, 16, 17, 20, 26]. Few investigations however, have been published which achieve low level analysis (µg/kg) typical of organochlorine contamination in native environmental samples [8, 10, 18].

This paper describes the application of automated SFE to native sewage sludge and marine sediment for the extraction of Organochlorine Pesticides (OCls) and Polychlorinated Biphenyls (PCBs) at µg/kg levels. The objective was to produce an efficient automated analytical procedure, from which UKAS accreditation could be achieved.

The method involved the extraction of 5–10 g portions of sample, extract clean-up and analysis by GC-MS using a double focusing mass spectrometer operated in SIR mode. The addition of copper granules to the bottom (exit) of the extraction cartridge was also included. This has been shown to remove sulphur contamination (4). Detection limits were estimated to be in the range of 0.5–10 µg/kg dry weight, depending on the matrix effects.

EXPERIMENTAL

Chemicals and Reagents

Certified standards were used for the preparation of calibration and spiking standards: PCB mixed stock, Dr Ehrenstorfer, 97.0 – 99.7% purity; OCl mixed stock, Dr Ehrenstorfer, 95.3 – 99.7% purity; trans heptachlor epoxide (OCl and PCB internal standard), Dr Ehrenstorfer, 99.0% purity. All solvents used were supplied by Rathburn Chemicals Ltd and were HPLC grade. All other reagents were analytical grade: alumina oxide, BDH Laboratory Supplies; silver nitrate, FSA Laboratory Supplies; florisil and sodium sulphate, Fisher Scientific; copper granules (-10+40 mesh), Aldrich 99.90% purity. The wet support matrix was supplied by Isco Inc.. Food grade liquid withdrawal carbon dioxide for SFE was supplied by BOC. Water was treated using an Elga Maxima system.

Sample and Cartridge Preparation

Contaminated harbour sediment obtained from the Firth of Forth, Scotland and sewage sludge samples taken from several East of Scotland Water sewage treatment works were used to develop the SFE methods. The procedures were validated using Standard Reference Material (SRM) 1941a, a marine sediment from the National Institute of Standards and Technology and Reference Material No. 392, a sewage sludge from the Community Bureau of Reference (BCR).

All samples were freeze-dried and homogenised by grinding with a blender or sieving. Approximately 5.0–10.0 g aliquots of homogenate were accurately weighed into the SFE cartridges and any remaining space filled with support matrix. The addition of 2- 3 g of copper granules to the bottom of the cartridge efficiently removed any sulphur present and avoided possible gross chromatographic interferences [4]. Support matrix (diatomaceous earth) was also used as blank sample material. Diatomaceous earth is an inert, large surface area material derived from the skeletons of diatoms [12].

Supercritical Fluid Extraction (SFE)

SFE was performed using an ISCO Automated SFX 3560 Supercritical Fluid Extraction System. This consists of an SFX 3560 extractor with a dual solvent-pumping system (syringe pump Model 260D), which can deliver a modified or a continuous flow of supercritical fluid. The analytes are collected in a temperature controlled liquid trap which is pressurised above ambient. The SFE also has a sophisticated restrictor device and is capable of extracting 24 samples per run.

SFE Method Development

The SFE method was developed using the contaminated harbour sediment extracted in duplicate. An initial method was optimised by varying selected parameters (see Table I). These parameters included extraction temperature, extraction pressure and percentage of dichloromethane modifier, by dynamic addition [9]. The optimised method was evaluated by extracting five replicate samples of the contaminated harbour sediment and marine sediment SRM 1941a, thus obtaining efficiency and precision data. Results for the contaminated harbour sediment were compared to 10 previously obtained Soxhlet extraction results.

The SFE method was then applied to spiked sewage sludge samples with the addition of 2% methanol modifier by dynamic addition. Sludge A was extracted in five replicate samples and sludge B in three replicate samples, both were spiked at 25 μg/kg dry weight. This modified method was also validated, by extracting five replicates of sewage sludge BCR No. 392.

TABLE I The Initial SFE Method showing the Parameters Varied During the Method Development Stage

Step	*Operation*	
1	Extraction chamber pressure (psi)	5000 – 7000
2	Extraction chamber temperature (°C)	60 – 100
3	Restrictor temperature (°C)	100
4	Collection temperature (°C)	5
5	Static extraction time (mins)	5
6	Restrictor flow rate (ml/min)	1.5
7	Set modifier volume %	0 – 10
8	Dynamic extraction time (min)	25
9	End program	
	Chamber wash time (sec)	90
	Number of vial washes	2
	Solvent replenish 0.5 ml every (min)	5.0
	Pressurized collection	on
	Precool collection vial	off
	Post heat collection vial (degas)	on
	Refill of pump during extraction	on
	Refill of pump before extraction	on
	* Solvent added before extract (ml)	10.0
	*Collection solvent: hexane	

Extract Clean-up Procedure

The clean-up of the sediment extracts was achieved by passing the extract through a 1.0 g alumina/silver nitrate and 3.5 g alumina column and eluting with 70 ml of hexane. The clean-up procedure, column and reagent preparation is given by the Department of the Environment [27]. Sludge extract clean-up involved a modification to the above method in which 1.5 g alumina and 2.0 g florisil replaced the 3.5 g alumina.

Analysis by GC-SIR-MS

GC-MS analysis was performed on a Micromass ProSpec with a Fisons 8060 GC. The injection method was direct cool on-column. The GC conditions were 60 °C (hold 1 minute) programmed to 180 °C at 25 °C/minute, then 3 °C/minute to 260 °C (hold 8 minutes) using a J&W DB-5, 60 m x 0.25 mm I.D column and a HP (uncoated, deactivated) retention gap 1 m x 0.52 mm I.D. A SIR scheme was developed for the analysis of 15 OCl compounds and 10 PCB congeners with two significant ions chosen for each analyte. Table II shows the selected masses and associated time windows.

TABLE II SIR Scheme for OCL + PCB Analysis

RT (min)	*Organochlorine Compound*	*SIR group*	*Time Window (min)*	*m/z 1*	*m/z 2*
14.23	Trifluralin	1	13.00 – 15.00	306.055	264.014
15.37	α-HCH	2	15.00 – 22.30	182.974	180.989
15.58	HCB	2		283.788	285.792
17.00	γ-HCH	2		182.974	180.989
19.20	# 28	2		255.968	257.963
19.25	# 31	2		255.968	257.963
21.02	# 52	2		291.936	289.939
22.00	Aldrin	2		264.908	262.908
23.28	Isodrin	3	22.30 – 25.00	262.864	194.996
24.21	Heptachlor epoxide	3		216.96	236.841
25.33	op-DDE	4	25.00 – 28.15	246.001	247.997
25.42	# 101	4		325.882	327.879
27.18	pp-DDE	4		246.001	247.997
27.36	Dieldrin	4		260.878	262.87
27.53	op-TDE	4		235.01	237.006
28.53	Endrin	5	28.15 – 30.20	262.863	264.859
29.11	# 149	5		359.883	361.833
29.19	# 118	5		325.882	327.879
29.49	pp-TDE	5		235.01	237.006
29.58	op-DDT	5		235.01	237.006
30.35	# 153	6	30.20 – 37.30	359.883	361.833
30.54	# 105	6		325.882	327.879
31.58	pp-DDT	6		235.01	237.006
32.14	# 138	6		359.883	361.833
36.35	# 180	6		393.8	391.797

RESULTS AND DISCUSSION

The results for the development of the SFE method can be seen in Tables III and IV. Each table displays the average amount of OCl or PCB extracted from the contaminated harbour sediment for the various extraction parameters. Included in both of these tables are the average Soxhlet results, obtained from 10 previous extractions of the harbour sediment over a number of years.

At 60 °C changes to the pressure seem to have little effect on the recovery of the organochlorine compounds. However at the higher temperature the analyte recovery is greater and shows a general increase as the pressure increases. These results demonstrate the temperature and pressure effects of the extraction process.

The extraction temperature and pressure control the density of the supercritical fluid. When the temperature is close to the critical temperature of the fluid and the pressure is high, the fluid will be at its highest density [1]. Under these conditions analyte extraction may at first appear to be optimum. However, the solvating effect of the supercritical fluid is related to both the density of the fluid and the volatility of the analyte [1]. Therefore, analytes with significant vapour pressures will have higher solubility at increased temperatures, as shown here.

The addition of modifier to supercritical fluid can enhance the recovery of analytes. The specific mechanism by which this is achieved is not fully understood. However, it is thought to alter analyte-matrix interactions [11], or compete with the analyte for the active sites on the matrix [1]. The data in Tables III and IV shows this effect. The addition of DCM modifier to the supercritical fluid resulted in an increase in the extraction efficiency for the lower extraction temperatures and pressures. At these temperatures and pressures increasing the modifier volume enhanced the analyte extraction further. However, at 7000 psi and 100 °C the opposite is seen with the extractability of the organochlorine compounds decreasing with the addition of the modifier. It has already been noted that the solvating effect at this temperature and pressure is high, so it is feasible that the addition of a modifier will have no significant effect on the analyte recovery. The reduction in analyte recovery with increased modifier addition could be attributed to a higher critical temperature caused by the mixing of the modifier and CO_2 [3].

The results indicate an extraction temperature of 100 °C and pressure of 7000 psi should be selected for the procedure. With these parameters 12 out of the 25 organochlorine compounds analysed exhibited improved extraction compared to Soxhlet results.

TABLE III SFE Method Development Results. Average OCl Conc. Extracted from the Contaminated Harbour Sediment

Extraction Details:			*OCl – average concentration extracted (μg/kg)*					
Temp. (°C)	*Pressure (psi)*	*% Modifier*	*HCB*	*γ-HCH*	*pp-DDE*	*Dieldrin*	*pp-TDE*	*pp-DDT*
* Soxhlet Extraction			153	1.8	32.8	7.6	8.5	2.9
60	5000		118	1.2	38.9	12.6	3.6	5.4
	6000		112	1.6	37.3	12.5	3.6	5.2
	7000		109	1.7	36.1	12.9	3.6	4.7
100	5000		137	1.8	42.7	15.1	4.8	5.2
	6000		145	2.5	44.3	15.8	5.3	5.3
	7000		185	1.2	49.7	17.8	5.9	7.0
80	6000	0	112	1.6	37.3	12.5	3.6	5.2
	6000	5	174	1.1	47.0	16.5	4.7	6.5
	6000	10	218	1.0	58.0	19.2	5.0	7.5
100	6000	0	145	2.5	44.3	15.8	5.3	5.3
	6000	5	179	4.0	41.4	17.4	5.8	6.7
	6000	10	179	2.3	35.7	16.5	5.6	8.5
80	7000	0	109	1.7	36.1	12.9	3.6	4.7
	7000	5	167	2.0	45.3	16.0	4.7	6.9
	7000	10	168	2.7	44.5	15.4	5.0	6.3
100	7000	0	185	1.2	49.7	17.8	5.9	7.0
	7000	5	180	3.1	36.1	16.5	5.4	5.7
	7000	10	160	2.5	32.1	14.1	4.5	7.2

* Soxhlet extraction for 4 hr with 60:40 hexane:acetone, followed by 1.0 g alumina/silver nitrate and 2.0 g alumina clean-up. Analysis by GC-ECD using on-column injection at 60 °C. The GC conditions were 60 °C (hold 1 min) programmed to 180 °C at 25 °C/min then 2 °C/min to 260 °C (hold 1 min) using a DB-5 60 m x 0.25 mm I.D. column and a HP (uncoated, deactivated) retention gap 2 m x 0.52 mm I.D.

The efficiency and precision of the analytical procedure was evaluated. Table V lists the results of the SFE compared to Soxhlet for the extraction of the contaminated harbour sediment. It is clear from the results that the recovery of the SFE extractions are not consistent with the Soxhlet extractions. The SFE results show high reproducibility in contrast to the Soxhlet results which show very poor precision. This is not indicative of current literature [4] and could possibly be explained by the presence of sulphur in the extracts, which may adversely effect separations and saturate the ECD detector.

TABLE IV SFE Method Development Results. Average PCB Conc. Extracted from the Contaminated Harbour Sediment

Extraction Details:			*PCB – average concentration extracted (µg/kg)*					
Temp. (°C)	*Pressure (psi)*	*% Modifier*	*28*	*101*	*118*	*153*	*138*	*180*
* Soxhlet Extraction			2.6	9.5	3.1	6.9	10.8	3.6
60	5000		3.6	2.5	3.1	3.4	4.9	5.5
	6000		3.2	2.5	3.0	3.2	4.5	6.5
	7000		2.1	2.5	2.8	3.0	3.7	6.1
100	5000		3.2	3.3	4.2	4.5	6.1	5.6
	6000		3.5	3.1	4.2	4.4	4.7	5.8
	7000		4.5	3.8	5.7	5.9	7.4	6.1
80	6000	0	3.2	2.5	3.0	3.2	4.5	6.5
	6000	5	3.5	3.4	4.9	5.0	7.2	8.1
	6000	10	5.0	4.6	5.7	5.6	9.6	5.2
100	6000	0	3.5	3.1	4.2	4.4	4.7	5.8
	6000	5	1.7	4.2	4.6	4.8	5.0	4.3
	6000	10	1.1	4.5	4.4	4.9	5.4	4.5
80	7000	0	2.1	2.5	2.8	3.0	3.7	6.1
	7000	5	3.2	3.7	4.6	5.6	6.8	7.6
	7000	10	1.7	3.9	4.1	4.8	6.5	5.6
100	7000	0	4.5	3.8	5.7	5.9	7.4	6.1
	7000	5	3.7	4.6	4.6	4.9	6.7	5.3
	7000	10	3.8	4.4	4.2	4.4	5.3	3.6

TABLE V Evaluation of the Accuracy and Precision of the Analytical Procedure. Comparision of SFE with Soxhlet Extraction for the Contaminated Harbour Sediment

Organochlorine Compound	*Soxhlet*		*SFE*		
	mean µg/kg dw†	*% RSD*	*mean µg/kg dw*†	*% RSD*	*% rec*‡
HCB	153	45.0	160	1.2	105
γ-HCH	1.8	52.7	2.0	5.1	111
pp-DDE	32.8	28.7	37.4	2.1	114
Dieldrin	7.6	31.1	18.9	2.6	249
pp-TDE	8.5	8.6	5.0	3.9	59
pp-DDT	2.9	37.6	8.2	6.2	283
# 28	3.0	87.0	4.0	13.8	133
# 101	9.5	13.1	3.6	3.7	38
# 118	3.1	59.1	4.9	5.0	158
# 153	6.9	17.5	5.9	5.7	86
# 138	10.8	24.2	8.5	7.4	79
# 180	3.6	21.6	4.1	5.2	114

† dw, dry weight. ‡ Recovery compared with Soxhlet extraction (100 %).

To complete the validation of the method the marine sediment SRM 1941a was analysed, the results are listed in Table VI. The results of our measurements are in agreement with the certified values. This demonstrates that the SFE method is reliable and has the capability of being applied to other sediment matrices.

TABLE VI Analysis of Marine Sediment 1941a

Organochlorine Compound	*SFE Results*		*Certified Results*	
	mean μg/kg dw[†]	*SD μg/kg dw*	*mean μg/kg dw*[†]	*SD μg/kg dw*
HCB	79.71	4.61	70.00	25.00
pp-DDE	6.23	0.53	6.59	0.56
# 28	6.73	0.65	9.8	3.7
# 31	4.72	0.31	6.2	2.4
# 52	8.16	0.90	6.89	0.56
# 101	11.20	1.40	11.00	1.60
# 149	10.45	0.96	9.20	1.10
# 118	8.50	0.53	10.00	1.10
# 105	3.63	0.49	3.65	0.27
# 138	12.28	1.02	13.38	0.97

[†] dw, dry weight.

The successful application of the SFE method to sewage sludge samples required the addition of 2% methanol modifier by dynamic addition. This was perhaps required to weaken the hydrophobic interactions between the organochlorine compounds and the sludge matrix. These interactions will be greater in sludge than sediment matrices due to its high organic nature, which will lead to accumulation of the highly lipophilic organochlorine compounds [28, 29].

Table VII shows the average recoveries and relative standard deviations derived from the two different sludge matrices spiked at 25 μg/kg, dry weight. The data for sludge B should be interpreted with care as it was extracted only in triplicate. Nevertheless, it is clear that the precision and recoveries obtained were excellent. The data for sludge A also shows good precision although the recoveries are considerably less. This is indicative of the problems associated with analysing environmental samples, where matrix effects can vary considerably from one sample to another [30, 31].

The validation results for extraction of sewage sludge BCR No. 392 are listed in Table VIII. The results of the SFE procedure are in close agreement with the certified values. The analytical method is therefore, very efficient for many sewage sludge matrices. However, where a reduction in extraction efficiency occurs due to matrix effects, detection limits may need to be increased.

TABLE VII Organochlorine Recovery and Precision Results for the SFE of Sewage Sludge Matrices

	Sludge A		*Sludge B*	
Organochlorine Compound	*mean % recovery*	*% RSD*	*mean % recovery*	*% RSD*
Trifluralin	75.1	6.5	139.6	3.9
HCB	36.0	15.1	105.0	7.1
pp-DDE	60.4	12.6	109.7	8.1
op-TDE	58.9	13.7	97.9	10.4
pp-TDE	52.9	14.0	91.5	6.2
pp-DDT	70.0	10.1	107.2	12.6
# 28	44.8	10.2	107.1	4.5
# 52	48.8	9.7	110.3	3.8
# 101	48.3	13.5	118.0	4.1
# 118	48.2	13.1	137.3	2.8
# 105	39.9	14.0	123.9	2.7
# 138	41.9	16.9	146.7	3.1

TABLE VIII Analysis of Sewage Sludge BCR No. 392

	SFE		*Certified Values*	
Organochlorine Compound	*mean µg/kg dw*[†]	*SD*	*mean µg/kg dw*[†]	*SD*
# 28	113.0	5.4	100	10
# 101	134.5	21.8	134	11
#118	94.9	10.5	97	12
# 153	283.8	10.3	288	18

[†] dw, dry weight.

CONCLUSIONS

This study demonstrates the use of SFE to produce an efficient and reproducible analytical method, for the extraction of organochlorine compounds from sediment and sludge matrices. Analyte recovery increased with extraction temperature and supercritical fluid density, but required the addition of methanol modifier for successful extraction in sewage sludge matrices.

This study demonstrates the problems associated with the analysis of environmental samples. Co-extraction of other compounds e. g. sulphur, can result in poor chromatography and matrix effects can reduce extraction efficiency, leading to variations in detection limits from sample to sample.

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