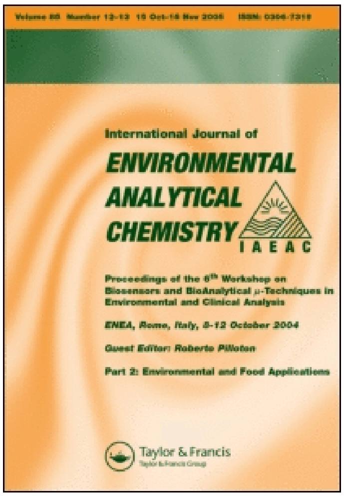

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# SUPERCRITICAL FLUID EXTRACTION OF ACIDIC HERBICIDES FROM SEDIMENT

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An improved method for the supercritical fluid extraction of seven acidic herbicides from sediment is described in which pentafluorobenzyl derivatives of the herbicides are formed within the extraction vessel through the addition of pentafluorobenzyl bromide, triethylamine and acetone to the sample prior to extraction. Parameters affecting the derivatisation reactions and extraction efficiency of herbicides from spiked sediment are discussed. Herbicide recovery shows a positive correlation with volume of acetone modifier added to the cell. Herbicide recoveries from sediment achieved with the supercritical fluid extraction—in-situ derivatisation (SFE-ISD) technique were significantly higher than those for a more traditional liquid extraction method. Recoveries from sediment spiked at 2 $\mu$g g$^{-1}$ range from 63% (2,4-dichlorophenoxyacetic acid "2,4-D") to 88% (4-chloro-2-methylphenoxypropionic acid "MCPP") with SFE-ISD, whereas the recoveries of the same compounds are only 31% and 35% respectively after liquid extraction with a 2:1:1:1 mixture of methyl tertiary butyl ether:acetone:hexane:heptane. The formation of halogenated derivatives enables the extracts to be analysed by the sensitive GC-ECD technique at ng g$^{-1}$ levels.

*Keywords:* SFE; in-situ derivatisation; chlorophenoxy herbicides; pentafluorobenzyl bromide; gas chromatography

## INTRODUCTION

The extraction of non-polar organic compounds from environmental matrices (soils and sediments) with supercritical carbon dioxide has well documented

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advantages in terms of speed, selectivity and the reduced consumption of organic solvent compared to traditional extraction techniques such as Soxhlet. Comprehensive reviews of the subject are available in the literature.[1, 2] However, the extraction efficiency of acid herbicides and other polar compounds with supercritical $CO_2$ is limited by their solubility in the relatively apolar extracting fluid and the fact that they may interact strongly with active sites on the sample matrix. In many circumstances the addition of an organic co-solvent (or "modifier") to the carbon dioxide increases the recovery of a compound by both increasing its bulk solubility in the extracting fluid and interacting with active sites on the sample matrix preventing analyte readsorption.[3]

Chemical derivatisation of analytes to make them more amenable to chromatographic analysis and/or to improve detection limits is a powerful analytical tool.[4] The addition of a derivatisation reagent to the extraction vessel prior to SFE allows for in-situ derivatisation, eliminating further sample preparation steps.[5-8] In-situ derivatisation also has the significant advantage of enhancing solubility of polar analytes in supercritical carbon dioxide and the (usually) polar reagents, present in excess, compete for binding sites on matrix surfaces releasing more analyte molecules.[5]

Up to 90% of 2,4-D was recovered as the methyl ester after 3 extractions of river sediment spiked with 20 $\mu g\ g^{-1}$ of 2,4-D prior to SFE with in-situ derivatisation using trimethylphenylammonium hydroxide (TMPA) (20% solution in methanol). In the same work,[6] similar recoveries of 2,4-D from soil could be achieved using a single extraction when a solution of 12% $BF_3$ in methanol was added to the extraction vessel. This is consistent with other results[7] where recoveries of 90% for a 10 $\mu g\ g^{-1}$ spike of 2,4-D in soil using (14%) methanolic $BF_3$ solution were reported. However, for routine analysis $BF_3$/methanol has practical limitations in that not all acid herbicides are derivatised[6] and corrosion has been observed in systems where PEEK tubing is used.[7]

Mixtures of chlorophenoxy herbicides (CPHs) were extracted from spiked soil and sand following derivatisation *in-situ* with various reagents (trimethylphenyl ammonium hydroxide, benzyltrimethylammonium chloride, benzyltriethylammonium chloride, tetrabutylammonium hydroxide/methyl iodide and pentafluorobenzyl bromide) prior to analysis by GC-MS.[8] The best recoveries were observed for the tetrabutylammonium hydroxide/methyl iodide combination (86-109% recovery for the majority of compounds spiked at 250 $\mu g\ g^{-1}$ on topsoil). Recoveries of CPHs from topsoil spiked at 1-3 $\mu g\ g^{-1}$ using pentafluorobenzyl bromide (PFBBr) ranged from 24% (2,4-D) to 83% (dicamba).

Whilst methylating reagents have been used to obtain good recoveries of acid herbicides from soils and sediments, the low ECD response of compounds

TABLE I The seven acidic herbicides analysed in this study.

| Abbreviation | Compound name |
|---|---|
| MCPP | 4-chloro-2-methylphenoxypropionic acid |
| MCPA | 4-chloro-2-methylphenoxyacetic acid |
| 2,4-DP | 2-(2,4-dichlorophenoxy)propionic acid |
| 2,4-D | 2,4-dichlorophenoxyacetic acid |
| 2,4,5-T | 2,4,5-trichlorophenoxyacetic acid |
| Bentazone | 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide |
| Benazolin | 4-chloro-2,3-dihydro-2-oxo-1,3-benzothiazol-3-ylacetic acid |

containing only one chlorine atom[9] limits the range of herbicides which may be analysed by the simple and sensitive gas chromatography-electron capture detection (GC-ECD) technique. The formation of pentafluorobenzyl derivatives results in significantly enhanced sensitivity to ECD allowing the direct chromatographic analysis of herbicide fractions containing compounds with 1 to 3 chlorine atoms derived from natural sediment samples.[10]

In this paper we discuss the factors controlling the efficiency of the derivatisation reaction and the extent of extraction of various acid herbicides (Table I) from spiked sediment samples using pentafluorobenzyl bromide. Factors such as extraction temperature, extraction pressure, extraction time and $CO_2$ flow-rate, mass of derivatising reagent added to the cell and the effect of organic modifier (static and/or dynamic) are discussed. Recoveries are compared to those obtained with a more traditional solvent extraction method.

## EXPERIMENTAL

### Reagents

Herbicide standards were obtained from Promochem (Welwyn, UK) and used without further purification. Pentafluorobenzyl bromide ($\alpha$-bromo-2,3,4,5,6-pentafluorotoluene) and triethylamine were obtained from Aldrich (Gillingham, UK). Potassium carbonate and anhydrous sodium sulphate (both Analar grade) were obtained from BDH Merck (Lutterworth, UK). All solvents were glass-distilled grade from Rathburn (Walkerburn, UK). Stock solutions of the herbicides were prepared in toluene at 1000 mg $L^{-1}$. Mixed herbicide solutions for spiking were prepared in acetone at 10 mg $L^{-1}$. Solutions of pentafluorobenzyl bromide (PFBBr) were prepared weekly at 5% or 10% (v/v) by dissolving 500$\mu$L or 1000$\mu$L in 10 mL acetone. All solutions were stored in the dark at 4°C. SFE grade carbon dioxide with a helium head pressure was supplied by Air Products (Crewe, UK).

## Sediment Samples

Samples of river sediment (organic carbon 5.1%, particle size: 20% "granules" [>2500 μm], 10% med.—coarse sand [100&-2500 μm], 35%—v. fine sand [71-250 μm], 35% silt and clay [<250 μm]) were air dried, and disaggregated gently with a pestle and mortar prior to use.

## Supercritical Fluid Extraction

Supercritical carbon dioxide extractions were carried out using a Suprex Prepmaster interfaced with a MPA-1 solvent modifier pump and Accutrap assembly (Suprex Corp., Pittsburgh, USA). Extractions were carried out with solid-phase trapping, analytes being collected onto a trap containing 1:1 octadecyl silica:silanised glass beads (Alltech, Carnforth, UK) maintained at 10°C during the extraction. The extract was eluted from the trap at 30°C with 4 mL acetone (flow-rate 1 mL $min^{-1}$). After prolonged use, the Accutrap was prone to blockage when relatively high masses of pentafluorobenzyl bromide were added to the extraction cell. In this situation analytes are lost as the carbon dioxide stream is vented from the instrument to avoid a dangerous pressure build-up. The blockages were caused by the precipitation of solid pentafluorobenzyl bromide as a result of cooling at the restrictor outlet. Therefore in some experiments the Suprex Accutrap was replaced by an Isco SFX coaxially heated adjustable restrictor (Isco Inc. Europe, Hengoed, UK). This restrictor can be heated to a temperature of 150°C along its entire length. During dynamic extraction the inlet heating block of the Isco restrictor temperature was 80°C and the temperature of the valve stem (inserted into 10 mL acetone trapping solvent) was 25°C.

In the initial experiments to determine the optimum conditions for the in-situ formation of herbicide derivatives, glass beads in a 5 mL stainless steel extraction vessel were spiked with 1 μg of each herbicide in acetone. The acetone was allowed to evaporate for five minutes prior to addition of PFBBr solution, triethylamine (TEA) and, in some cases, static modifier. The volumes of derivatising reagents used were 120 μL and 30 μL for PFBBr (5% v/v in acetone) and TEA respectively. The derivatising reagent was therefore present in excess relative to the herbicides (50 nmol PFBBr compared to 36 nmol herbicides). Extractions were carried out at temperatures ranging from 80°C to 120°C and pressures of 250 Atm to 450 Atm for 20 minutes in static mode and 20 minutes in dynamic mode with a flow-rate of 1.5-2.5 mL $min^{-1}$. The optimum extraction conditions (temperature, pressure, flow-rate and modifier content) were then used to extract herbicides from sediment spiked with ca. 2 μg $g^{-1}$ of each compound. The mass of derivatising reagent added to the cell and derivatisation reaction times were varied (20-100 mg and 5-30 minutes respectively) to achieve maximum recovery from sediment. Extractions with ca. 20 and 40 mg PFBBr were carried out with 5% (v/v) solution in acetone (240 and 480 $\mu$L respectively). Extractions with ca. 60, 80 and 100 mg PFBBr were carried out with 10% (v/v) solution (360, 480 and 600 $\mu$L) due to limitations on the void space within the cell. Triethylamine was added at volumes equivalent to 3 $\mu$L per mg of PFBBr. Duplicate extractions were performed with the exception of the 100 mg experiment (4 extractions).

## Liquid Extraction Methods

The liquid extraction method used in this study was an adaptation of that described by Sattar and Paasivirta[11] for the extraction of 4-chloro-2-methylphenoxyacetic acid (MCPA) and its metabolites from soil samples. Samples of dried sediment (3g) were spiked with herbicides (ca. 2 $\mu$g $g^{-1}$) and mixed well before being transferred to Nalgene extraction bottles (100 mL). Anhydrous sodium sulphate (2g) was added prior to acidification with orthophosphoric acid (3mL, 1N). After waiting for any gas generation to cease (15 minutes) the sediment was extracted with 50 mL of a 2:1:1:1 mixture of methyl tertiary butyl ether-:acetone:hexane:heptane for 40 minutes on an end-over-end shaker. The extract was filtered (Whatman 41 filter paper) and a further 50 mL of solvent as added to the extraction bottle and the extraction repeated. The combined extracts were rotary evaporated (Büchi Rotavapor) to ca. 4 mL before transfer to a screw top test tube where the remaining solvent was removed under a gentle stream of oxygen free nitrogen. Acetone (4mL) was added to the tube followed by pentafluorobenzyl bromide (120 $\mu$L, 1% v/v in acetone) and 30 $\mu$L of aqueous potassium carbonate solution (30% w/v). The tubes were left for 24 hours in the dark at room temperature. The acetone solution containing herbicide PFB derivatives was then treated in the same way as the SFE extracts (see below).

## Sample Clean-up

Preliminary studies showed that the extracts obtained by either SFE or liquid extraction required purification to remove both co-extracted contaminants and derivatisation by-products prior to analysis by GC-ECD. The method employed was a modification of that previously described.[10] Briefly, the acetone solutions were reduced to 2 mL under a gentle stream of oxygen free nitrogen, 2 mL of 2,2,4-trimethylpentane (TMP) was added and the mixture blown down to 1 mL. A further 2 mL of TMP was added and the blow-down procedure repeated. The possibility of the loss of herbicide derivatives was minimised by ensuring that the solutions were never taken to dryness.

The TMP solution and up to 2 mL hexane washings was passed through 1 g (5 cm) 5% deactivated silica packed into a disposable Pasteur pipette and topped with 0.5 cm anhydrous sodium sulphate. Contaminants were eluted with toluene/ hexane (1:3, 5 mL) and the acid herbicide derivatives eluted with toluene (8 mL). Further dilution with toluene was necessary for GC-ECD analysis, to achieve a final concentration of herbicides in solution of 0.002 to 0.01 ppm. Both standard solutions for GC calibration and sediment extracts were treated in the same way, therefore, any losses that did occur from the sediment extract would be compensated by similar losses from the standard solutions.

### GC-ECD

Purified extracts were analysed on a Carlo Erba 4200 gas chromatograph via split/splitless injection onto a BP-5 column (SGE, Milton Keynes, UK), length 25m, i.d. 0.33 mm, film thickness 0.5 μm. The GC oven temperature was programmed from 75°C (injection temperature, held for 2 minutes) to 150°C at 30°C $\text{min}^{-1}$, then 8°C $\text{min}^{-1}$ to 285°C which was held for 10 minutes. The carrier gas was helium at a pressure of 0.9 kg $\text{cm}^{-2}$, (flow-rate 3.4 mL $\text{min}^{-1}$) the ECD make-up gas was nitrogen. Quantitation was achieved by external calibration with solutions of derivatised standards in the range 0.002 ppm to 0.01 ppm.

## RESULTS AND DISCUSSION

### Optimisation of Derivatisation Conditions Using an Inert Matrix

The trapping efficiency of the Suprex Accutrap ranged from 97.1% (rsd 8.5%) for MCPP to 99.6% (rsd 13.7%) for 2,4,5-T at a collection temperature of 10°C after 30 minutes dynamic extraction with carbon dioxide containing 10% acetone at a flow-rate of 2.5 mL per minute. These values were obtained by spiking a solution of pre-derivatised herbicides onto silanised glass beads packed into the SFE extraction vessel. Similarly, trapping efficiencies were determined for the Isco heated restrictor using 10 mL acetone as the collection solvent. The temperature of the restrictor inlet block was maintained at 80°C and the temperature of the valve stem (inserted into the acetone) was 25°C. After 30 minutes extraction at a flow-rate of 0.3 to 0.45 mL $\text{min}^{-1}$ the trapping efficiency ranged from 92.8% (rsd 7.7%) for 2,4-DP to 97.3% (rsd 0.36%) for MCPA.

The relative efficiency of the derivatisation reaction under different temperature and pressure conditions was inferred from the recovery of pentafluorobenzyl esters from glass beads spiked with the parent compounds and a solution of the derivatisation reagents after 20 minutes reaction. There was no apparent relationship between the temperature or pressure of the reaction cell and the recovery of the herbicide derivatives. This is illustrated by Figure 1 which shows the mean recovery of the seven herbicides at the nine different T/P conditions employed. Spiking was undertaken withwith 1 $\mu$g of each parent compound, 120 $\mu$L pentafluorobenzyl bromide solution (5% v/v in acetone) and 30 $\mu$L triethylamine. Extractions took place for 20 minutes in static mode and 20 minutes in dynamic mode at 100°C, 450 Atm and a flow-rate of 2.5 mL $min^{-1}$ unmodified carbon dioxide. Solid phase trapping at 10°C. 3 mL extraction vessel.

The highest mean recovery was observed at an extraction temperature of 80°C and pressure of 350 Atm ($CO_2$ density 0.79 g $ml^{-1}$). Recoveries of the individual compounds ranged from 99% (2,4,5-T) to 36% (2,4-D). The recovery of MCPA was also low at 41%. (This wide range of herbicide derivatisation efficiency is

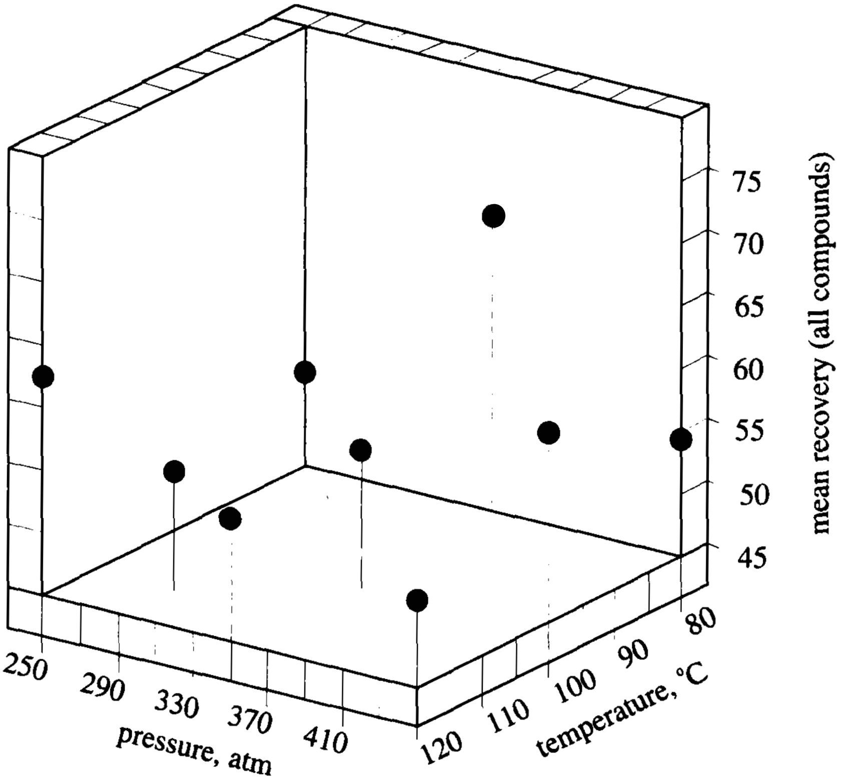


FIGURE 1 The effect of temperature and pressure on the mean recovery of the 7 herbicide pentafluorobenzyl derivatives from spiked glass beads.

reflected in the relative standard deviation for herbicide recovery of 36% of the mean.) The recoveries of 2,4-D (48%) and MCPA (47%) were highest at a reaction temperature of 100°C and pressure of 450 Atm ($CO_2$ density also 0.79 g $ml^{-1}$). The mean recovery of all seven herbicides was somewhat lower at 60%, but the variability of compound recoveries was also much lower, as indicated by a relative standard deviation of 15%. Individual compound recovery ranged from 47% (MCPA) to 69% (Benazolin). Although 100°C/450 Atm was not the optimum reaction condition for the pentafluorobenzylation of all compounds it was considered that the combination of relatively good recoveries for most compounds and potential for enhanced release of analytes bound to soil and sediment surfaces at relatively high temperature/pressure conditions made this the most favourable extraction condition.

Because adsorption interactions of the herbicides with the glass beads matrix should be minimal and the trapping of the analytes is efficient, the poor extraction efficiencies of the compounds (and hence poor derivatisation efficiencies) are probably caused by limited solubility of the parent herbicides in supercritical $CO_2$. The solubility of 2,4-D in supercritical $CO_2$ is reported to be low,[12] but it could be improved by saturating the fluid with water, i.e. the addition of a polar co-solvent. If solubility in supercritical $CO_2$ is a limiting factor on the derivatising efficiency of acid herbicides with PFBBr, the addition of a polar co-solvent (or "modifier") to the extraction vessel should increase the solubility of the polar acid herbicides in the extracting fluid and therefore increase derivatisation yield.

Acetone was chosen as the co-solvent due to its polarity, its volatility (allowing easy removal at the end of the extraction) and the fact that it is a very good solvent for pentafluorobenzyl bromide. Experiments were carried out for 20 minutes each in static mode and dynamic mode (flow-rate 2.5 mL $min^{-1}$) at 100°C and 450 Atm with 120 $\mu$L 5% (v/v) PFBBr and 30 $\mu$L triethylamine added to glass beads spiked with 1 $\mu$g of each of the acids and 0, 250 or 500 $\mu$L acetone. The addition of up to 500 $\mu$L acetone to the extraction vessel significantly increases the recovery of the herbicide derivatives (Figure 2) suggesting that herbicide solubility in the extracting fluid is indeed a controlling factor on derivatisation reaction efficiency. Figure 2 also shows that the addition of 10 mole % acetone to the supercritical carbon dioxide during the dynamic extraction step further increases the recovery of most of the herbicide PFB esters. This may result from the enhanced solubility of the derivatives in the extracting fluid which would, in turn, lead to their more efficient removal from the extraction cell. The mean ($n = 3$) recoveries of herbicide PFB derivatives from glass beads at 100°C and 450 Atm with 500 $\mu$L acetone static modifier and 10 mole % acetone dynamic modifier were: MCPP 91% (rsd 4.2%); MCPA 74%

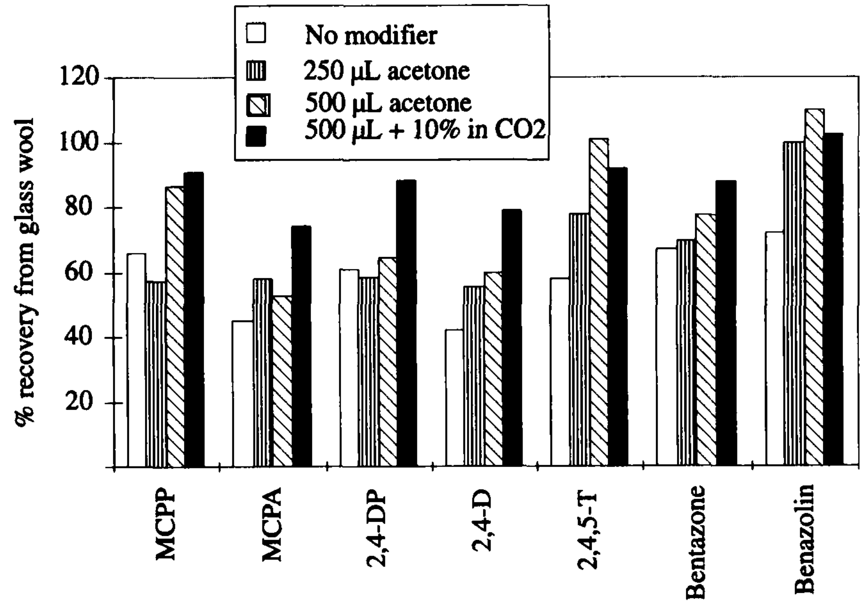


FIGURE 2 The effect of increasing acetone modifier addition on the derivatisation and extraction efficiency of acidic herbicides from spiked glass beads.

(rsd 4.2%); 2,4-DP 88% (rsd 3.0%); 2,4-D 79% (rsd 3.6%); 2,4,5-T 92% (rsd 2.3%); Bentazone 88% (rsd 6.5%); Benazolin 102% (rsd 2.0%).

## The Extraction of Herbicides from Spiked Sediment

Experiments with an inert matrix showed that the volume of acetone static modifier added to the extraction vessel had a significant effect upon the recovery of the herbicide derivatives. Figure 3 confirms that this is also the case for the in-situ derivatisation and extraction of the same compounds from river sediment spiked at 2 $\mu g\ g^{-1}$ (extraction conditions: T = 100°C, P = 450 Atm., 30 minutes static extraction, 30 minutes dynamic extraction, flow-rate 0.3 to 0.5 mL $min^{-1}$ with 10 mole % acetone in carbon dioxide, liquid trapping into 10 mL acetone with an Isco SFX heated restrictor; 5 mL extraction vessel, ca. 4.5g sediment). It can be seen that there is no correlation between the amount of derivatising reagent added and the recovery of the herbicide derivatives. A positive correlation is apparent between the total volume of acetone added to the cell and herbicide derivative recovery. Note that the volume of acetone present in the cell has a greater impact on herbicide derivative recovery than does the mass of pentafluorobenzyl bromide (PFBBr).

A significant increase in recovery of chlorophenoxy herbicides as their PFB esters from spiked topsoil (1-3 $\mu g\ g^{-1}$ per compound) was noted[8] when using 1000 $\mu L$ of 5% (v/v in acetone) PFBBr solution compared to the recoveries with 250 $\mu L$ PFBBr; e.g. 2,4-D recovery increased from 1.9% to 23.7%. It would appear likely that the improved herbicide recovery noted by these workers is a result of the additional volume of acetone present.

Although the mass of PFBBr present in the extraction cell is of secondary importance compared the volume of acetone, it is advantagous to use a large excess of derivatising reagent in order to ensure that all the herbicides in an unknown sample are derivatised. For this reason it was decided to add 100 mg PFBBr (600 $\mu L$ of 10% v/v solution in acetone) to sediment samples (ca. 4.5g) in the subsequent method development.

The effect of reaction (static extraction) time on the recovery of herbicide derivatives from river sediment (spiked with 2 $\mu g\ g^{-1}$ of each herbicide) was

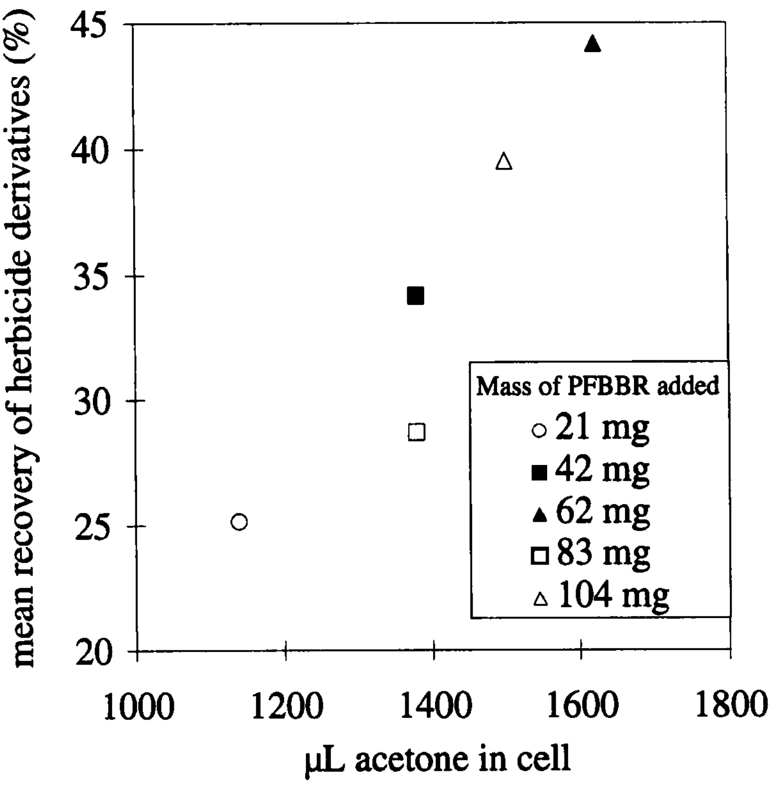


FIGURE 3 Mean recovery of herbicide derivatives from sediment (spiked with 2 $\mu g\ g^{-1}$ of each parent compound) shows a systematic increase as the volume of acetone in the cell increases.

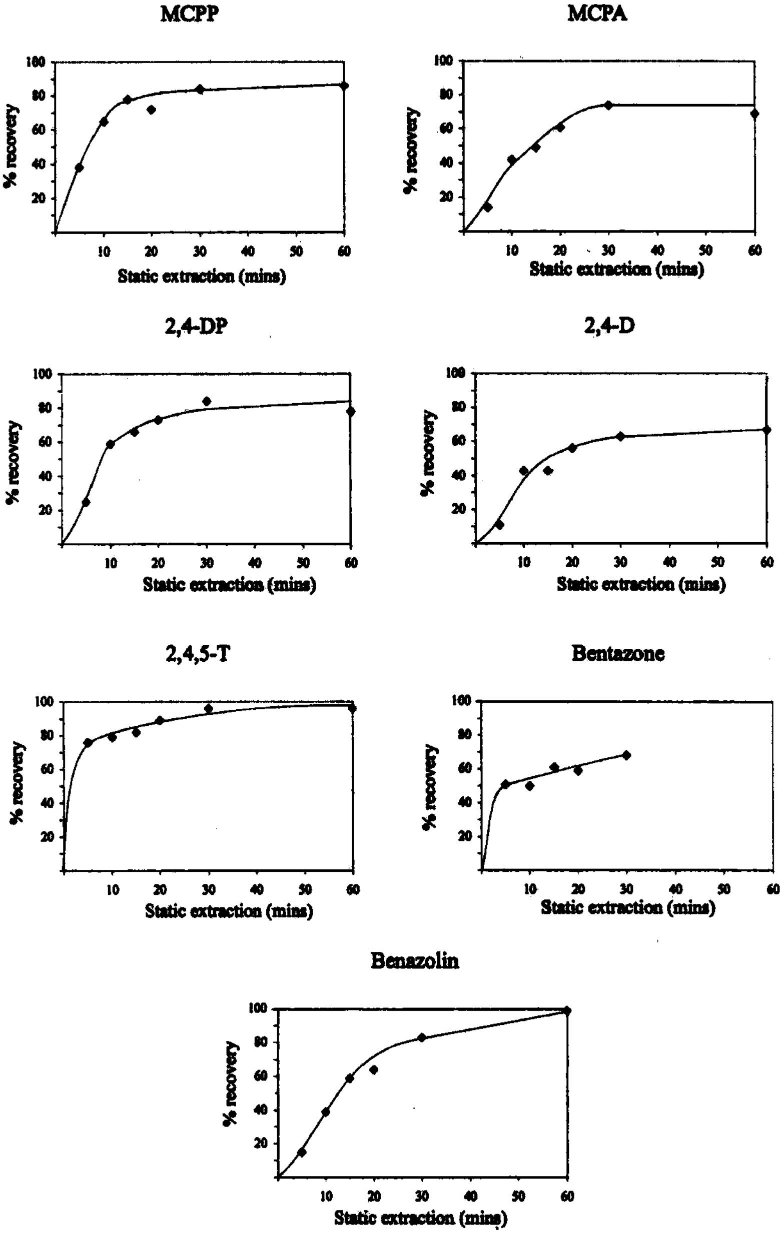
investigated using the maximum volume of acetone modifier and derivatising reagents which could be physically added to the cell (900 $\mu$L acetone static modifier, 600 $\mu$L 10% PFBBr in acetone and 300 $\mu$L TEA). Static extraction times were increased from 5 minutes to 30 minutes whilst dynamic extraction times were maintained at 30 minutes with a flow-rate of 2.5 mL min$^{-1}$. The results are shown in Figure 4 (extraction conditions: T = 100°C, P = 450 Atm., 5 minutes to 30 minutes static extraction, 900 $\mu$L acetone static modifier, 30 minutes dynamic extraction, flow-rate 2.5 mL min$^{-1}$ with 10 mole % acetone in carbon dioxide, solid phase trapping; 5 mL extraction vessel, ca. 4.5g sediment). The derivatisation of bentazone and 2,4,5-T appears to proceed more quickly than for other compounds, with 51% and 76% of these herbicides recovered (respectively) after only 5 minutes derivatisation. The recovery of all herbicide derivatives increases with increasing reaction time, although the rate of increase slows as reaction time lengthens. Increasing the static extraction (reaction) time above 30 minutes has little effect on herbicide derivative recovery for all compounds except benazolin.

The important role of acetone static modifier in increasing herbicide derivatisation and subsequent extraction from spiked sediment was shown earlier. The effect of acetone modifier during dynamic extraction is demonstrated in Figure 5 which shows the mean recoveries of the 7 herbicides. These experiments were conducted with liquid trapping (10 mL acetone) at a flow-rate of 0.3 mL min$^{-1}$. The mean cumulative recovery of the compounds after dynamic extraction with 17 mL of supercritical carbon dioxide (equivalent to 3.5 cell volumes) is 48% without dynamic modifier (experiment A), and 73% when 10 mole % is added to the $CO_2$ in dynamic mode (experiment B). The latter value is extremely close to the mean recovery of 74% obtained for solid phase trapping at a flow-rate of 2.5 mL min$^{-1}$ under otherwise the same extraction conditions.

The optimum conditions for the recovery of the acid herbicides from sediment were therefore:

| | |
|---|---|
| Extraction temperature | 100°C |
| Extraction pressure | 450 Atm. |
| Extraction time | 30 minutes static; 30 minutes dynamic |
| Static modifier | 900 $\mu$L acetone |
| Dynamic modifier | 10 mol% acetone |
| Derivatising reagents | 600 $\mu$L PFBBr (10% v/v in acetone), 300 $\mu$L triethylamine |
| Dynamic extraction flow-rate | 2.5 mL min$^{-1}$ (solid phase trapping)<br>0.3 mL min$^{-1}$ (liquid trapping) |

Table II compares the recovery of the herbicides from river sediment using the SFE parameters described above, to the recovery obtained with the solvent extraction method described by Sattar and Paasivirta.[11] It is apparent that the



MCPP

MCPA

2,4-DP

2,4-D

2,4,5-T

Bentazone

Benazolin

FIGURE 4 Recovery of the individual herbicide derivatives from sediment (spiked with 2 $\mu g\ g^{-1}$ of each parent herbicide) as a function of the static extraction time.

recovery of herbicides is substantially increased with the SFE method when compared to the more traditional solvent extraction technique.

Although the recoveries of the herbicides are not quantitative, they represent a substantial improvement on previous work to form halogenated derivatives[8] suitable for analysis by GC-ECD. The sensitivity of this analytical method means that detection limits of less than 10 ng $g^{-1}$ in sediment are feasible if 4g of sediment is extracted. Using the method developed in this study we have already detected the 7 acid herbicides at concentrations of 20 ng $g^{-1}$ in spiked sediment with analysis of the extracts by GC-ECD and confirmation by GC-mass spectrometry. Previous work on the supercritical fluid extraction of acid herbicides from environmental matrices[6-8] has involved relatively high spike levels (up to 250 $\mu$g $g^{-1}$). SFE with in-situ derivatisation by PFBBr and analysis by GC-ECD offers the possibility of acid herbicide analysis at the much lower concentrations typically found in natural samples.

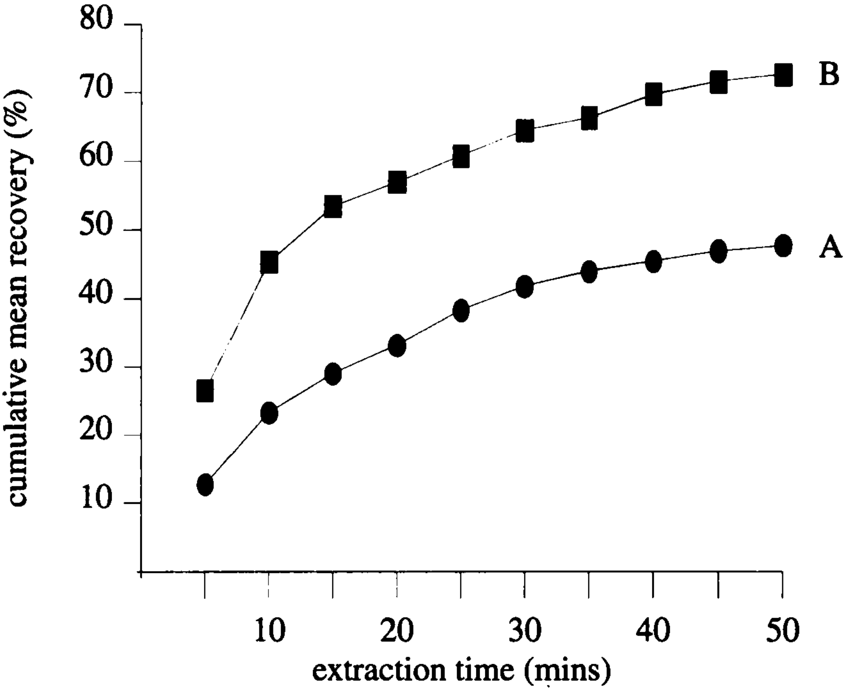


FIGURE 5 Mean herbicide recovery from sediment spiked at 2 $\mu$g $g^{-1}$ using, A: 900 $\mu$L static acetone modifier only; B: 900 $\mu$L static acetone modifier plus 10 mole % dynamic acetone modifier. Other extraction conditions as in Figure 4.

TABLE II Comparison of the recovery of herbicides from river sediment (spiked at 2 $\mu g\ g^{-1}$) using SFE and liquid extraction methods. Extraction conditions are described in the text.

| % recovery of compound from spiked sediment SFE Method(n = 4) | | | Liquid Extraction Method(n = 3) | |
|---|---|---|---|---|
| | Mean | RSD | Mean | RSD |
| MCPP | 88 | 16 | 39 | 13 |
| MCPA | 65 | 9.6 | 31 | 17 |
| 2,4-DP | 77 | 8.7 | 47 | 17 |
| 2,4-D | 63 | 6.6 | 36 | 18 |
| 2,4,5-T | 83 | 4.0 | 62 | 15 |
| Bentazone | 68 | 13 | 54 | 17 |
| Benazolin | 72 | 4.8 | 29 | 13 |

## CONCLUSIONS

The results obtained in this study indicate that supercritical fluid extraction with in-situ derivatisation with pentafluorobenzyl bromide and triethylamine achieves significantly improved recoveries of acidic herbicides from spiked sediment compared to an established liquid extraction method. Recoveries of herbicide derivitives range from 63% to 88% after only 1 hour extraction. An additional derivatisation step is required for the products of the liquid extraction method to achieve much lower herbicide recoveries (29% to 62%).

The amount of acetone static modifier added to the cell was shown to play a crucial role on the efficiency of the derivatisation reaction when using an inert matrix in the SFE extraction cell. This effect was interpreted as a consequence of increased analyte solubility in the extracting fluid. In addition, the presence of 10 mol% acetone dynamic modifier was found to increase the mean recovery of the 7 herbicides from sediment from 48% to 73%. This significant improvement is most likely to be caused by more efficient displacement of the herbicide derivatives from the extraction vessel.

Increasing the amount of pentafluorobenzyl bromide in the extraction cell (up to 100 mg) also increased the recovery of herbicide derivatives, however, it appeared that this was of secondary importance compared to the volume of acetone static modifier added to the cell.

### *Acknowledgements*

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