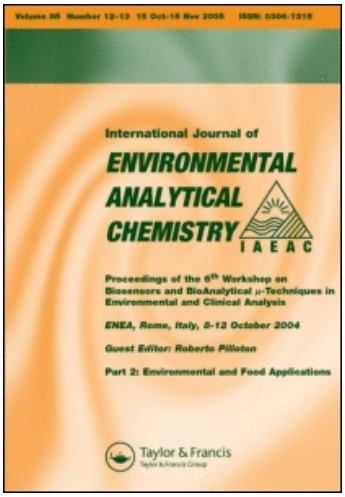

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DETERMINATION OF TRIALKYL AND TRIARYL PHOSPHATES IN SEDIMENT USING MICROWAVE EXTRACTION AND PACKED-CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY

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Trialkyl and triaryl phosphates (TAPs) are widely used as flame retardants in plasticizers and hydraulic fluids. A microwave extraction method used to isolate these compounds from harbour sediment was developed and compared with traditional Soxhlet and shake-flask techniques. Microwave extraction proved to be 15 times faster than the traditional methods and resulted in higher recoveries for non-polar TAPs. Another advantage of the method is a significant saving in organic extraction solvents and energy. For the analysis of microwave extracts, packed-capillary supercritical fluid chromatography (PC-SFC) coupled with thermionic detection was used. It is shown that by using density programming faster analyses and lower limits of detection, can be obtained than with isoconfertic SFC. Detection limits of TAPs in sediment extracts were 0.10–0.20 mg/kg. The method showed good reproducibility and linearity over three orders of magnitude.

KEY WORDS: Trialkyl and triaryl phosphates, microwave extraction, harbour sediment, supercritical fluid chromatography, packed-capillary columns, thermionic detection.

INTRODUCTION

Trialkyl and triaryl phosphates (TAPs) have been of environmental interest since the 1930s when outbreaks of polyneuritis in the United States were attributed to these compounds[1]. TAPs are extensively used in plasticizers (PVC) and hydraulic fluids to replace polychlorinated biphenyls (PCBs) as flame retardands[2]. The estimated global production of TAPs is approx. 77×10^6 kg per annum[3]. A large amount is eventually released into the environment. TAPs are found in river, ground[4–6] and drinking[7,8] water, and as a result of their low water solubility and high adsorption to particulate matter[1] they are also found in sediment[9–11]. Due to bioaccumulation TAPs are found in fish at levels 1,000 times higher than the concentra-

tions to which these were exposed[2,9]. In general, TAPs for industrial use exhibit low acute lethality in standard tests with mammals and birds; LD50 (oral) values for rats are 3–12 g/kg for the most toxic triaryl (e.g., triphenyl and tricresyl) phosphates[1]. However, tri-o-cresyl phosphate (TOCP) was found responsible for delayed neurotoxic effects in cattle[12] and delayed neurotoxicity occurred at levels of 1–2 g/kg in hens[1].

TAPs can be separated with either liquid (LC), gas (GC) or supercritical fluid (SFC) chromatography. The compounds lack specific UV absorbance and native fluorescence, but LC in combination with atomic-absorption detection can be used[13]. By miniaturizing LC systems it is possible to use GC-type (e.g., flame photometric or thermionic) detectors for the determination of TAPs[14,15]. TAPs can also be determined with GC, because they are thermally stable and sufficiently volatile[1,4,8], but the most polar ones, like trimethyl phosphate (TMP), tend to cause problems due to active sites on the stationary phase. TAPs have been determined with open tubular capillary SFC (OTC-SFC) using flame-ionisation detection (FID)[16]. Thermionic detection (TID), however, has the advantage of high selectivity for phosphorus-containing compounds. A TID can be coupled relatively easily to a packed-capillary SFC (PC-SFC) system and can be used with modified carbon dioxide as the mobile phase, which is not possible when using an FID[17]. PC-SFC offers shorter analysis times than does OTC-SFC and allows the injection of larger volumes[18]. The advantages of SFC over LC are clear; SFC is faster, more efficient, has no toxic mobile phase waste and next to the LC-type detectors, the more sensitive and selective GC-type detectors can be used. Nowadays SFC equipment is commercially available, and the technique increasingly becomes an interesting alternative to GC[19].

TAPs can be extracted from sediment by means of Soxhlet or shake-flask extraction[9]. In recent years, microwave irradiation has become popular because of its speed and simplicity. In addition to the fact that sample preparation with microwave irradiation normally is at least 10 times faster than the traditional methods[20–22], degradation of compounds occurring during traditional extraction processes can be avoided. Other advantages of using microwave sample preparation techniques are the smaller amounts of energy and solvents needed and the automation potential[23]. Microwave irradiation is a fast way of heating samples. To avoid the release of toxic and corrosive fumes, closed vessels can be used. The danger of explosion due to pressure build up, can be overcome by using strong, microwave-transparent and chemically inert vessels[23]. Nowadays, microwave sample digestion techniques for elemental analysis are frequently performed with closed vessels using elevated temperatures and pressures. However, when organic compounds have to be extracted, they may well be decomposed together with the matrix. This can be prevented by using open-vessel techniques. Samples are mixed with an appropriate solvent and irradiated, while avoiding boiling, for a certain period of time. After cooling and successive irradiation (to increase analyte recovery), the samples are centrifuged and an aliquot of the resulting supernatant is analysed[20,24]. Most of the microwave procedures published are destruction methods for elemental analysis[25–27]. Microwave destruction is used for complex matrices, such as waste water, sediment, blood, plastics and metal alloys; Feinberg[21] reviewed and classified over 770 applications of microwave destruction. Microwave irradiation can also be used for peptide and protein hydrolysis[28] and for thawing of biological samples[29] without significant degradation of the analytes, which may occur during thawing at room temperature or by

heating. So far not much has been published on extraction methods for organic compounds. Although microwave irradiation has been reported to be a useful extraction method[24,30], only Ganzler et al.[20,22] and, very recently, Onuska et al.[31] published microwave methods for crude fat, glucosides, pesticides and drug metabolites in different matrices.

In this paper PC-SFC coupled with a TID is used for the determination of TAPs. By programming the pressure and/or the temperature it is possible to vary the density and, consequently, the solvation of the analytes in the supercritical fluid during the run. In this way TAPs can be separated faster than by using a constant density. The disadvantage of density programming is the increasing background current which can be a problem when low analyte concentrations have to be determined; in OTC-SFC coupled with a TID this was found to be a limiting factor[17]. It is demonstrated that in PC-SFC this problem is easily overcome by peak compression which, actually, is a result of density programming too. Open-vessel microwave extraction is compared with Soxhlet and shake-flask extraction. Analyte recovery is investigated as a function of the number of microwave irradiation cycles to obtain optimum sample-preparation conditions. Since an extraction method should be able to release environmental pollutants which have been sorbed to a matrix for prolonged periods of time, the influence of incubation time on the recovery of TAPs spiked to harbour sediment was studied.

EXPERIMENTAL

SFC-TID instrumentation

The system set-up has been described in an earlier study[17]. A Phoenix-20 syringe pump (Carlo Erba Strumentazione, Milan, Italy) was used for mobile phase delivery and pressure control. All samples were introduced manually, through a 100 nl Valco injection valve (Type CI4W, Schenkon, Switzerland) positioned just outside the thermostatted waterbath. Fused-silica columns (120 × 0.32 mm I.D.) were slurry packed with LiChrosorb RP-18 (7μm) material which was obtained from Merck (Darmstadt, Germany). The column temperature was controlled by a thermostatted waterbath at 61°C. A 100 μm frit restrictor (Dionex/Lee Scientific, Salt Lake City, UT, USA) used for pressure restriction was shortened to give a flow rate of 10 μl min^{-1} at 150 bar. The restrictor was connected directly to the column and situated in the detector base of a Carlo Erba NPD-40 TID which was described by Verga[32]. The detector base was kept at 300°C by an Ether type 17-90B heat controller. The TID was connected to a Model 180 electrometer (Carlo Erba Strumentazione); for data acquisition a Varian 4400 integrator (Walnut Creek, CA, U.S.A.) was used. After optimization as described in[17], the hydrogen and air flow rates were set at 30 ml min^{-1} and 270 ml min^{-1}, respectively; the distance between the rubidium bead and the jet tip was 1.9 mm. It was necessary to cool the syringe of the Phoenix pump during the filling procedure in order to obtain maximum filling percentages. This was done by slightly releasing the nut at the front of the syringe and allowing the carbon dioxide to expand adiabatically. A known volume of modifier (methanol) was added to the syringe. The resulting percentages (expressed as % mol mol^{-1}) were calculated with interpolated

carbon dioxide densities at various temperatures, taken from the tabulated data of Angus et al.[33], and the known densities of methanol.

Extraction methods

Sediment samples were taken from a harbour in Rotterdam (Kortenoordsehaven). The amount of water in the sediment was determined by drying overnight at 105°C, and found to be 61% (w/w). The samples were homogenised by extensive stirring. Aliquots of 10 g (wet weight) were transferred to 20 ml screw-cap vials (Packard Instrument, Groningen, The Netherlands) and spiked by adding appropriate amounts of standard mixtures of the TAPs in hexane followed by homogenization. All spikes were made at the 5.0 mg/kg level, unless indicated otherwise. The spiked samples were incubated at room temperature for 0.5 to 35 days before analysis.

A simple microwave oven (Panasonic, Model NN-5452 B, 2450 MHz, 900 W, Matsushita Electric, UK) was used. The homogeneity of the microwave field was checked by the decolouration pattern of a layer of $CuSO_4.5H_2O$ crystals in a petri dish after 10 min of microwave irradiation at full power, as described by Ganzler et al.[22]. This pattern was taken into consideration when positioning the samples in the microwave oven. Microwave extraction was performed by adding 7.5 ml of the extraction solvent mixture to the samples. Three samples were placed in the microwave oven and irradiated for only 9 s to avoid boiling; next they were cooled to room temperature in 2–3 min and shaken to obtain good matrix-to-solvent contact.

Shake-flask extraction was performed with the same amount of extraction solvent as used in the microwave method. The vials were shaken vigorously for 4 h at room temperature with a home-made shaking apparatus which had a shaking frequency of 150 cycles min^{-1}.

After microwave or shake-flask extraction, 4.00 ml of water were added to the extracts and after 10 min centrifugation at 3500 rpm, 4.00 ml of the organic layer were transferred to a clean screw-cap vial. To these aliquots 0.50 ml of 2-propanol was added and subsequently the samples were slowly evaporated under a stream of dry nitrogen to ca. 0.5 ml, after which 2.00 ml of hexane were added. Before injecting 100 nl of the final extract into the SFC-TID system, a known amount of a TAP which was not included in the spiking mixture was added to the extract for volume correction.

Soxhlet extraction was performed by placing a sample, including the incubation vial, in a Soxhlet thimble which was positioned in a Soxhlet extractor. The samples were extracted for 4 h with 100 ml of the extraction solvent. Next, the extracts were evaporated to a volume of ca. 5 ml in a rotary evaporator. To these extracts 0.5 ml 2-propanol was added and the extracts were further treated as in the microwave and shake-flask methods (see above).

Chemicals

Carbon dioxide (99.97%) was obtained from Hoek Loos (Schiedam, The Netherlands). HPLC-grade ethyl acetate, hexane and 'Baker'-grade dichloromethane were obtained from J. T. Baker Chemicals (Deventer, The Netherlands). HPLC-grade methanol and 2-propanol

were purchased from Rathburn (Walkerburn, Scotland, UK). Trimethyl phosphate (TMP), triethyl phosphate (TEP), tri-n-propyl phosphate (TPP), tri-n-butyl phosphate (TBP) and triphenyl phosphate (TPhP) were all 99 % pure and came from Aldrich Chemie (Brussels, Belgium). Analytical grade tri-o-cresyl phosphate (TOCP) was a gift from A. Verweij (TNO, Rijswijk, The Netherlands). All solutions of TAPs were made in hexane and stored in a refrigerator. No change in concentrations was observed over a period of 6 months.

RESULTS AND DISCUSSION

Analysis of trialkyl and triaryl phosphates

The separation of TAPs was studied using SFC-TID with a conventional silica-based C-18 LC-type packing material and carbon dioxide modified with methanol as the mobile phase. The retention of TAPs increases with decreasing polarity of the analytes. The separation of the two compounds with the smallest polarity difference, TMP and TEP, requires both a relatively low pressure and organic modifier (methanol) percentage. Under these conditions the retention of the non-polar analytes becomes rather large. By programming the pressure, and, consequently, the mobile phase density solvation of the analytes can be varied, which results in a considerable reduction of the analysis time. A negative effect of density programming is the increasing background current which can cause problems when low analyte concentrations have to be determined. Fortunately, this problem is overcome by the peak compression effect which occurs for all the analytes, but especially for the later eluting compounds, since the capacity factors decrease because of increasing density. The advantages of density programming in PC-SFC, over isoconfertic separation, are obvious when comparing the chromatograms of Figures 1A and B, which were both recorded using TID detection. Figure 1C shows a typical gas chromatogram of TAPs, also with TID detection. The more polar compounds now have broad and tailing peaks, which is caused by interaction with the active sites of the GC column. With LC-TID it was not possible to separate TMP and TEP; the total analysis time being 30 min[14]. Therefore, we decided to determine TAPs with density-programmed SFC-TID.

Analytical data of TAPs in hexane

Detection limits of TAPs in hexane (signal-to-noise, ratio 3:1) were 3 to 50 pg (Table 1). Without density programming the limits of detection were 10 times higher for the polar TMP and 100 times higher for TOCP and TPhP (also see Figures 1A and B). For TMP and TEP calibration plots from the limits of detection (3 and 5 pg) up to 6 and 20 ng, respectively (8 data points, n=2) were linear; above this level they became very slightly curved. The other tested TAPs had linear calibration plots (11 data points, n=2) over three orders of magnitude (Table 1). For injected amounts 10-fold higher than the detection limits, the repeatability (peak area) was 3–8% (n=10; mixture of 6 TAPs injected on one day); the reproducibility was 4–9% (n=2 × 10; mixture of 6 TAPs injected on two separate days).

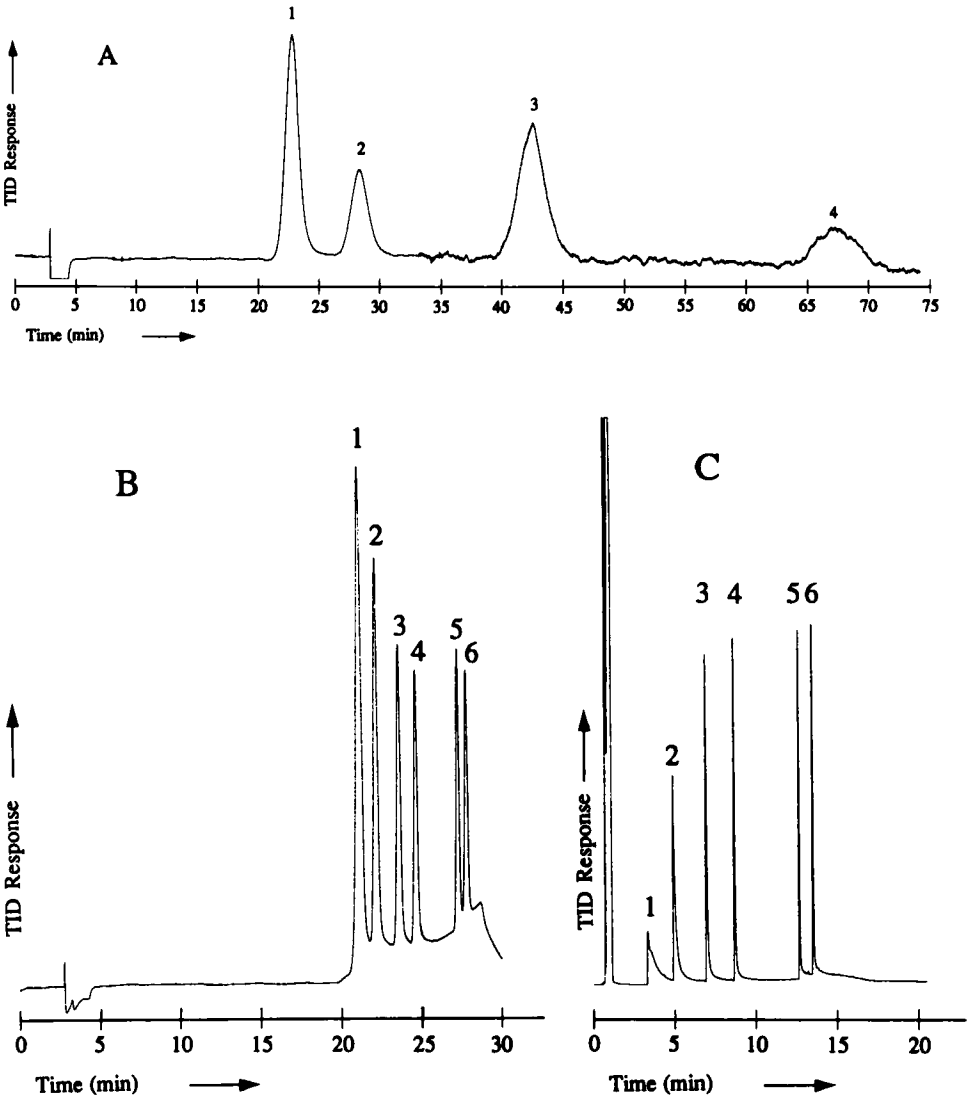

Figure 1 Comparison of SFC and GC using 6 TAPs as test analytes. (A) Isoconfertic SFC. Conditions: 100 nl injected; column, 115 × 0.32 mm I.D. packed with 7 µm LiChrosorb RP-18; mobile phase, carbon dioxide modified with 1.7 mol% methanol at 61°C; pressure, 112 bar; detector range, 12.8 pA full scale and after 33 min 3.2 pA full scale. (B) Pressure-programmed SFC. Same conditions as in A except for: pressure programme: 0 min, 112 bar; 19.5 min, 112 bar; 28.5 min, 238 bar; 31.5 min, 112 bar and detector range, 25.6 pA full scale. (C) Temperature-programmed GC. Conditions: Varian 3300 GC, septum-equipped programmable injector; 1.0 µl injected, injector temperature: 0.5 min at 40°C; 25°C/min; 2 min at 260°C; 25 m Supelco SE-54 column, 0.32 mm I.D., 0.45 µm film thickness; column temperature: 1 min at 40°C; 20°C/min; 3 min at 280°C; Varian TSD detector at 300°C; bead current, 3.2 A; detector range, 1024 pA full scale. Peaks: (1) 5.6 µg/ml TMP, (2) 5.8 µg/ml TEP (3) 6.1 µg/ml TPP, (4) 6.3 µg/ml TBP, (5) 6.1 µg/ml TPhP, (6) 6.6 µg/ml TOCP.

Table 1 Calibration data for trialkyl and triaryl phosphates in hexane[1].

Analytes	*Limit of detection [S/N=3] (pg)*	*Highest injected amount (ng)*	*Calibration curve* $y=a(\sigma_a)x+b(\sigma_b)$	R^2
TMP[2]	3	5.6	y = 73 (2) × + 93 (81)	0.998
TEP[2]	5	19.3	y = 62 (2) × + 174 (153)	0.999
TPP[3]	8	30.4	y = 62.8 (0.7) × + 120 (73)	0.999
TBP[3]	10	31.4	y = 58.7 (0.6) × + 60 (74)	0.999
TPhP[3]	50	50.8	y = 38.3 (0.4) × + 23 (75)	0.999
TOCP[3]	50	55.0	y = 38.8 (0.4) × + 88 (86)	0.999

[1] Column: 120×0.32 mm I.D. packed with 7 μm LiChrosorb RP-18. Mobile phase: carbon dioxide modified with 1.8 mol% methanol at 61°C. Pressure programme: 0 min, 123 bar; 20 min, 123 bar; 28.5 min, 242 bar; 32 min, 123 bar.
[2] 8 data points in duplicate.
[3] 11 data points in duplicate.

Optimization of the microwave extraction method

In order to be able to achieve good reliability during sample processing, the homogeneity of the microwave field was tested by irradiating $CuSO_4.5H_2O$ crystals for 10 min at full power. The vials used in the microwave extractions of TAPs were placed in positions having the same decolouration and thus the same irradiation intensity.

With pure hexane as extraction solvent it was only possible to extract the non-polar TAPs. Therefore, the more polar ethyl acetate and dichloromethane were both included in the extraction mixture to extract the polar TAPs as well, as suggested by Muir[1]. However, a high percentage of dichloromethane will interfere with the chromatography and especially with the detector background; therefore; it has to be removed prior to SFC. This can be done by evaporating the extracts to dryness and subsequently redissolving them in hexane. However, some of the TAPs were partly lost during this procedure, as was also observed by Muir et al.[9]. By adding 0.5 ml of 2-propanol, which has a relatively low vapour pressure, to the extracts and, next, evaporating the solution to ca. 0.5 ml, analyte losses due to evaporation were minimized and could be controlled, which resulted in standard deviations of less than 8% (n=10) for all solutes. For volume correction a known amount of a TAP (TBP) which had not been included in the spike, was added before injecting the extracts into the SFC-TID system.

The microwave extraction was optimized for the extraction of three samples at a time, although for a high sample throughput the whole microwave cavity can of course be used. With open vials the time of irradiation should be short to prevent evaporation of the (corrosive) extraction liquids which will make quantification difficult. Boiling of the extracts was observed after 15 s of irradiation; because evaporation may be assumed to start earlier, the samples were irradiated for only 9 s and then cooled to room temperature. The recovery of TAPs was studied as a function of the number of irradiation cycles; an example is shown in Figure 2. For a proper estimate of the gain in recovery due to microwave irradiation it is also necessary to determine the recovery without irradiation, instead of extrapolating to zero, as was done in an early microwave extraction study[20] because the recovery without

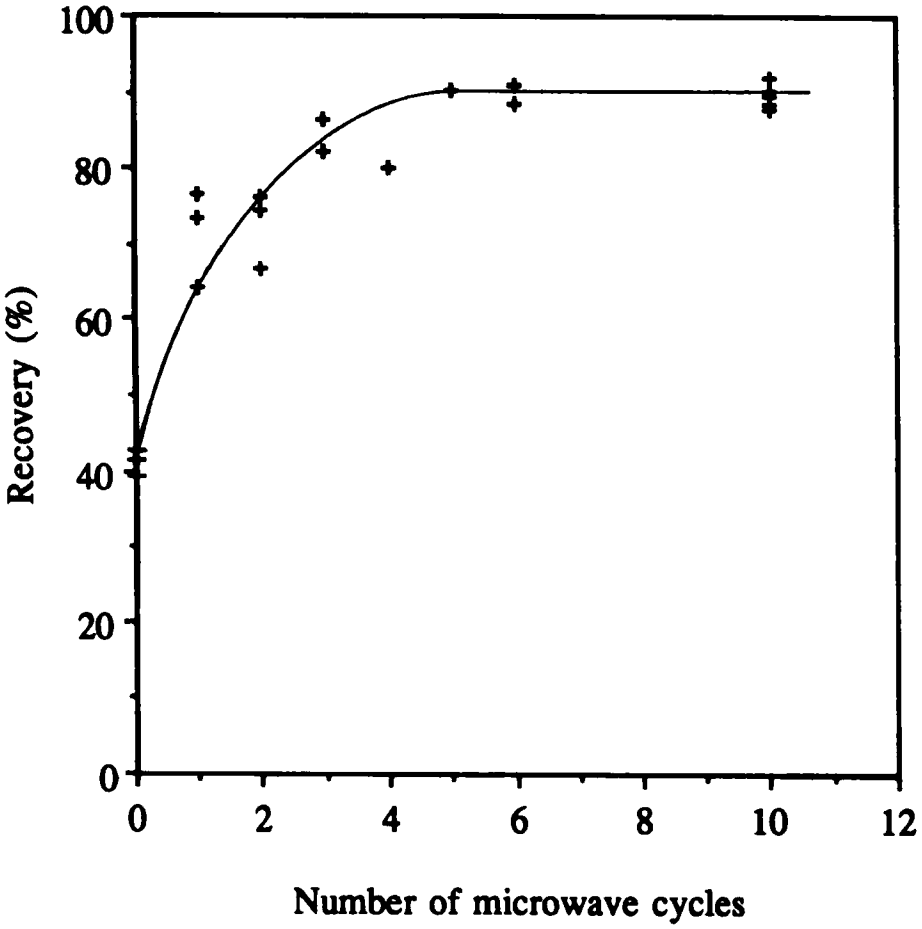

Figure 2 Recovery of TPP as a function of the number of microwave irradiation cycles. Spiking level: 5.0 mg/kg on sediment; 28 days of incubation.

microwave irradiation is not zero (Figure 2). For the compounds studied the recovery found without microwave irradiation was 44–82% of the recovery obtained using microwave extraction. In all instances six successive irradiation cycles were sufficient to reach plateau conditions. During the first extraction cycle the recovery increases 40–80% compared with the recovery without microwave irradiation, and by using five more cycles an extra gain of 10–30% is found.

Effect of incubation time on recovery

In order to study the effect of the incubation time after spiking on the recovery of the TAPs using microwave extraction, spikes dissolved in a small volume of hexane were added to

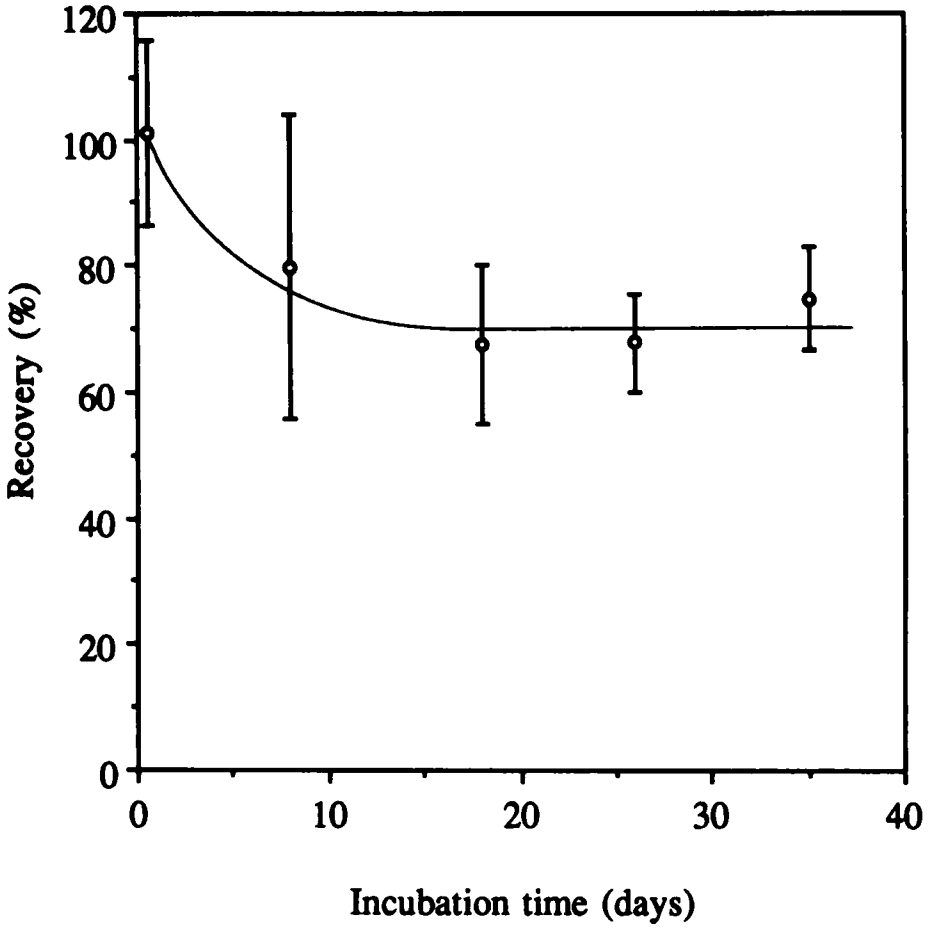

Figure 3 Effect of incubation time on the microwave extraction recovery of TOCP. Spiking conditions: 5.0 mg/kg on sediment, 10 microwave irradiation cycles. Data points: n=6; bar indicates standard deviation.

the wet samples. The samples were incubated at room temperature and homogenized every day. Figure 3 shows for TOCP that the recovery first decreases rather rapidly and becomes constant after about 15 days; the other TAPs showed a similar behaviour (data not shown). This result clearly illustrates the importance of letting analytes adsorb onto the matrix of interest for a rather prolonged period of time before studying an extraction technique. In other words, the experimental conditions used during spiking and sample storage should always be reported in appropriate detail, and should be sufficiently realistic.

All experiments presented in this paper were performed after incubation times of at least 18 days.

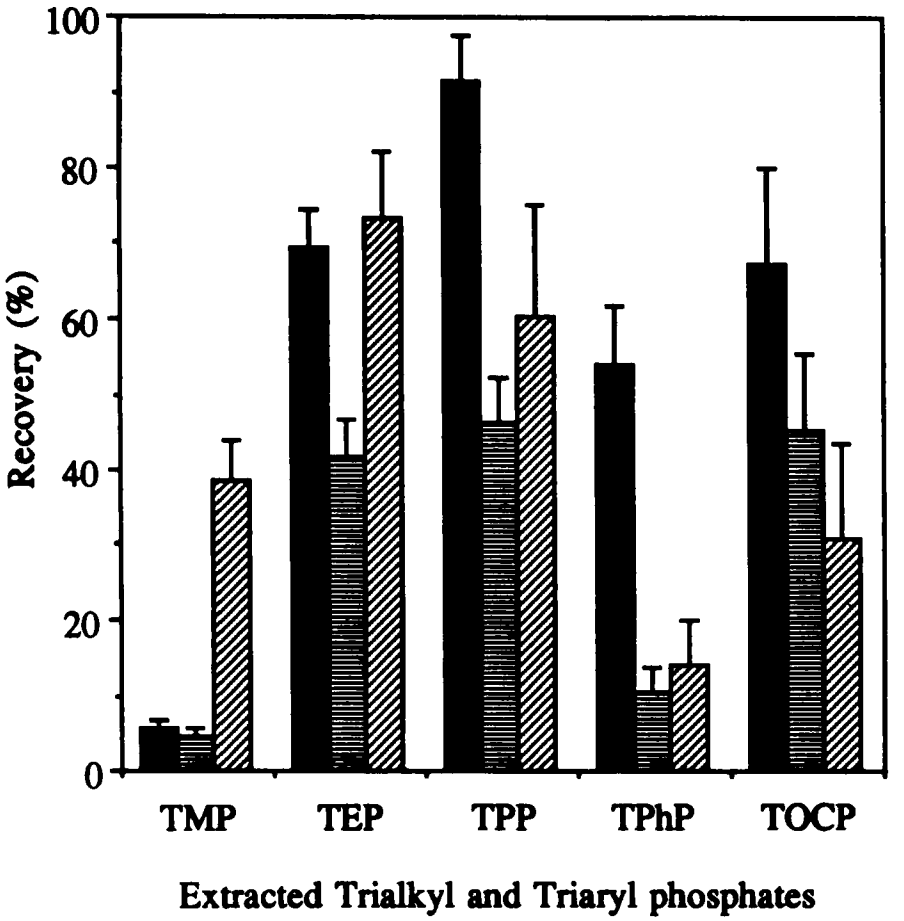

Figure 4 Comparison of microwave and traditional extraction techniques of TAPs from sediment. Spiking conditions: 5.0 mg/kg on sediment, 18 days of incubation. Data points: n=6; bar indicates the standard deviation. ■ microwave, ▤ shake-flask, ▨ Soxhlet.

Comparison of microwave extraction and traditional methods

The microwave extraction procedure was compared with shake-flask and Soxhlet techniques. In order to enable a fair comparison between the three techniques a solvent mixture containing the same proportions of hexane, dichloromethane and ethyl acetate, was used. Figure 4 shows the recoveries found with the various techniques. Microwave extraction gave better results than the shake-flask technique for all analytes. The Soxhlet technique gave a significantly higher recovery than the microwave method for a simple compound, viz. TMP. The low recovery of TMP using microwave extraction was not due to degradation during storage, as the incubation time studies did not show a continuously decreasing recovery.

The extraction efficiency of the TAPs also depends on their water-organic solvent partition coefficients. The relatively higher recovery for TMP using Soxhlet extraction can probably be explained on this basis, since the ratio water/organic solvent is considerably lower with the Soxhlet extraction as compared with the other techniques because of the significantly higher amount of organic solvent used with that technique.

The most important reason for preferring microwave extraction is its speed. The total time of extraction with microwave irradiation is only 15 min, which is about 15 times faster than with the traditional methods. Another advantage is the reduction of the solvent consumption from 100 ml with Soxhlet extraction to 7.5 ml with the microwave technique.

Analytical data for microwave extracts of TAP spiked sediment

An SFC-TID chromatogram of the microwave extract of a sample spiked with 0.30 mg/kg of five TAPs is shown in Figure 5. The tailing solvent peak was caused by a small amount

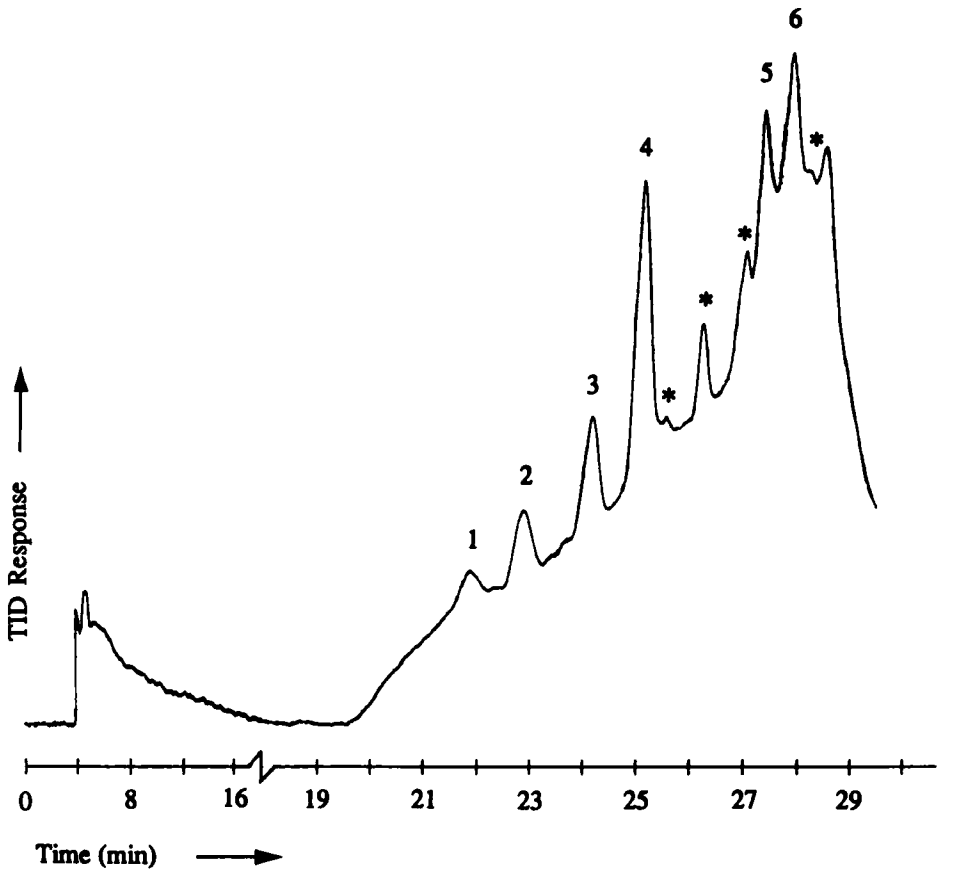

Figure 5 Typical SFC-TID chromatogram of a microwave extract. Spiking level: 0.30 mg TAPs/kg on sediment. Pressure programme: 0 min, 112 bar; 19.5 min, 112 bar; 28.5 min, 238 bar; 31.5 min, 112 bar; detector range, 26.4 pA full scale. Conditions: 19 days of incubation, 10 microwave irradiation cycles. Peaks: (1) TMP, (2) TEP, (3) TPP, (4) TBP internal standard, (5) TPhP, (6) TOCP, (*) Co-extracted compounds.

Table 2 Calibration data for trialkyl and triaryl phosphates extracted from harbour sediment using the microwave technique[1].

Analytes	*Limit of determination [S/N=3] (μg/kg)*	*Highest spiking level (mg/kg)*	*Calibration curve*[2] $y=a(\sigma_a)x+b(\sigma_b)$	R^2
TMP	200	500	y = 81 (1) × + 76 (86)	0.999
TEP	120	500	y = 358 (2) × + 367 (384)	0.999
TPP	100	500	y = 396 (5) × + 52 (563)	0.997
TPhP	160	500	y = 240 (8) × + 862 (1317)	0.994
TOCP	100	500	y = 257 (4) × + 810 (569)	0.997

[1] Column: 120 × 0.32 mm I.D. packed with 7 μm LiChrosorb RP-18. Mobile phase: carbon dioxide modified with 1.8 mol% methanol at 61°C. Pressure programme: 0 min, 123 bar; 20 min, 123 bar; 28.5 min, 242 bar; 32 min, 123 bar. 19 days of incubation, 10 microwave irradiation cycles.
[2] 12 data points in duplicate.

of dichloromethane left in the extract, but this did not interfere with the separation. The determination limits were 0.10–0.20 mg/kg for all test solutes (Table 2). The increasing limits of detection found with increasing molecular weight of the TAPs (Table 1), were not found for the TAPs in sediment extracts (Table 2); this is at least partly due to differences in recovery (cf. Figure 4). Spikes were made from the limits of determination (100–200 μg/kg) up to 500 mg/kg (12 data points, n=2). The variation in the slope was in all cases smaller than 3.2%. For extracts with concentrations 10-fold higher than the determination limits, relative standard deviations in peak area of 8–20% for the repeatability (n=6), and 9–25% for the reproducibility (n=2×6) were found.

All extractions (ca. 300 samples) were performed using the same microwave oven; the microwave energy and the homogeneity of the microwave field did not alter during this study. The SFC-TID system remained in perfect working order, and no changes in retention times and analyte detectability were observed. The variation in the modifier percentages were very small (<0.1%) and did not affect the retention times and separation of the TAPs as the applied pressure programme has a significantly greater influence on the analyte solubility in the mobile phase.

CONCLUSIONS

Density programming in PC-SFC has the advantages of faster analysis and lower limits of detection compared to isoconfertic SFC. Next to the higher injection volumes which can be used, these are further reasons for using PC-SFC instead of OTC-SFC for the determination of TAPs.

The recoveries of the TAPs spiked on sediment—which depended on the incubation time between spiking and extraction—found with microwave extraction were comparable with, or better than those found using traditional methods. Although the irradiation of samples is more efficient when more water is present, the recovery of polar compounds such as TMP will be lower when the analytes have to be extracted into an organic phase. The speed of the

microwave procedure is its main advantage; only 15 min were necessary to reach plateau conditions as against several hours when using traditional methods. The relatively small amounts of solvent and energy needed are other reasons for preferring the microwave technique.

The combined microwave extraction SFC-TID procedure for TAPs in harbour sediment showed good reproducibility. The limits of determination were 0.10–0.20 mg/kg, and good linearity was observed from the limit of determination up to 500 mg/kg on sediment. The robustness of the total analytical procedure was fully satisfactory: some 300 sediment samples were analysed without any maintenance being required.

Microwave extraction protocols for organic compounds are not available at present. They should be developed to facilitate introduction of the technique in (environmental) laboratoria. These protocols should give guidelines with regard to extraction solvent (e.g., polarity, acidity. and vapour pressure), optimum irradiation time, number of irradiation cycles and further sample handling (e.g., clean-up, concentration and analysis) for the determination of a compound in a certain matrix.

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