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Pressurised hot water extraction coupled on-line with liquid chromatography–gas chromatography for the determination of brominated flame retardants in sediment samples

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Abstract

Pressurised hot water extraction (PHWE) was coupled on-line with liquid chromatography–gas chromatography (LC–GC) to determine brominated flame retardants in sediment samples. After extraction with pressurised hot water the analytes were adsorbed in a solid-phase trap. The trap was dried with nitrogen and the analytes were eluted to the LC column, where the extract was cleaned, concentrated and fractionated before transfer to the GC system. The fraction containing the brominated flame retardants was transferred to the GC system via an on-column interface. The PHWE–LC–GC method was linear from 0.0125 to 2.5 μg with limits of detection in the range 0.70–1.41 ng/g and limits of quantification 6.16–12.33 ng/g.

Keywords: Pressurised hot water extraction; Extraction methods; Flame retardants; Sediment; Environmental analysis; Halogenated compounds

1. Introduction

Flame retardants are compounds that are added to polymers, paints and textiles to improve their fireproof properties. The main applications are in plastic housings of electronic products such as television sets and computers in car parts and in electrical components and cables. Included among the different groups of flame retardants are inorganic chemicals, organic phosphate esters with and without halogens, and chlorinated and brominated organic compounds. Bromine-based compounds comprise an estimated 30% of the volume of all flame retardants employed [1–3].

Brominated flame retardants (BFRs) are a structurally diverse group of compounds, including aromatics, cyclic aliphatics, phenolic derivatives, aliphatics, phthalic anhydride derivatives and others. The most common brominated flame retardants are tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDE), hexabromocyclododecane (HBCD) and polybrominated biphenyls (PBBs) [2–4]. PBBs and PBDEs have many properties in common with polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs), which make them long-lived, bioaccumulating, environmental pollutants. The water solubilities and vapour

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pressures of PBBs, TBBPA, HBDE and PBDEs are very low [2], causing them to be adsorbed rapidly onto solid particles of sediment and soil when released into the environment. The impact on health and the environmental characteristics of brominated flame retardants are not very well known. The acute toxicity of most of the compounds seems to be fairly low, but some have shown similar toxic effects to PCBs, PCDDs and polychlorinated dibenzofurans [5].

The analytes in sediments tend to be very tightly bound to the sample matrix and effective methods of extraction are required. Brominated compounds in sediment have usually been extracted by liquid–solid extraction [6–9] and Soxhlet extraction [10]. These traditional methods have a number of drawbacks, however; not only is the extraction time-consuming but the large volumes of organic solvents that are required must later be evaporated to concentrate the extract. Recently, environmentally friendly and fast extraction methods such as supercritical fluid extraction (SFE) and pressurised hot water extraction (PHWE) have been successfully applied to the extraction of organic pollutants, including BFRs from a variety of sample matrices [11–18]. At 200–350°C, which is the temperature range usually used in PHWE, water is a good extraction solvent for nonpolar compounds [13–15]. Temperature is the main parameter controlling the physicochemical parameters of water, the extracted analytes and the extraction rate, efficiency and selectivity. The high temperature significantly alters the solvent properties of water, especially the dielectric constant (ε), and enhances the solubility of less-polar compounds dramatically [19]. Pressure, on the other hand, has only a minor effect on the dielectric constant of water. When nonpolar compounds are extracted, low values of ε are desirable [14].

After the extraction step, sample clean-up is required in the analysis of BFRs in environmental samples because matrices are complex and analytes are present in only trace amounts. Typically, the extraction method is not sufficiently selective and the extract contains a large number of matrix compounds, which may co-elute with the analytes and disturb the quantitative analysis. Sediment samples, for example, contain inorganic compounds such as elemental sulphur and relatively high concentrations of various hydrocarbons, which would interfere with the GC analysis of the BFRs. The extract thus has to be purified, fractionated and concentrated before the final analysis. Sample pretreatment, however, is not only laborious but it is the most error-prone part of the analysis. Contamination, analyte loss and reduced reliability are general problems with any multi-step procedure.

A number of attempts have been made to analyse solid samples for pollutants by coupling SFE or PHWE directly to a GC system. Unfortunately, the on-line coupling of extraction to large-volume GC is usually impossible because many extracts of environmental samples are very dirty. However, using LC as a clean-up step between the extraction and GC steps allows the whole analysis to be made in a closed system. The LC is used for extract clean-up and fractionation and the final analysis is done by GC. Coupling of PHWE on-line to LC–GC has been used successfully for the analysis of polycyclic aromatic hydrocarbons (PAHs) in sediments [18].

In this study, an on-line combination of PHWE and LC–GC was developed for the analysis of sediment samples for brominated flame retardants. The linearity and the limits of detection and quantification of the developed PHWE–LC–GC method were determined and the method was applied to the analysis of real sediment samples.

2. Experimental

2.1. Reagents and samples

All solvents were of HPLC quality. *n*-Pentane, acetone, toluene and ethyl acetate were from Lab Scan Analytical Sciences (Dublin, Ireland). *n*-Pentane was distilled in the laboratory before use to remove impurities. Isooctane was from Rathburn (Walkerbur, UK). Water was distilled and deionised before use. Acid-washed sea-sand was from Riedel-de Haën (Seelze, Germany) and it was refluxed for 6 h in acetone–heptane (1:1, v/v), filtered, and dried in an oven before use. The internal standards, 4,4′-dibromooctafluorobiphenyl and 2,2′-binaphthyl, were from Aldrich (Gillingham, UK) and AccuStandard (New Haven, CT, USA), respectively. The bromi-

nated standards [mixture of hexabromobiphenyl (BP6) and heptabromobiphenyl, mixture of tribromotrichlorocyclohexane, tetrabromodichlorocyclohexane and pentabromochlorocyclohexane, pentabromotoluene, tetrabromobisphenol A (BP4A), tetrabromophthalic anhydride (PHT4) and tris(2,3-dibromopropyl)phosphate (T23P)] were all technical mixtures from AccuStandard. All standards were prepared in toluene, except hexabromobiphenyl, which was prepared in isooctane. Further dilutions were made in pentane or pentane–ethyl acetate (85:15, v/v).

The samples used for the fractionation study in LC were a sample consisting of 0.5% of gasoline (95 octane rating, JET, Finland) in pentane and a 1.0 μg/ml standard mixture of 17 PAH compounds (AccuStandard) prepared in pentane. All samples were injected from a 20-μl sample loop to the LC system. Analytes were detected with UV detection (MicroUVIS 20, CE Instruments, Milan, Italy).

The sediment samples used in the study were JML [collected from the Baltic Sea (59°34.89′N/23°37.83′E) 19 October 1998, particle size 5–10 cm] and 1529:1 (collected from the Vistula River, site Kiezmark near Gdansk, 6 June 1992, particle size 0–10 cm). Sediment JML was provided by Dr. H. Kankaanpää (Finnish Institute of Marine Research, Helsinki, Finland) and sediment 1529:1 by Dr. B. van Bavel (Institute of Environmental Chemistry, University of Umeå, Umeå, Sweden). The sample size used in sediment extractions was 100 mg. Before the sample was placed in the extraction vessel, the sediment was mixed with 1 g sea sand. Finally, the vessel was filled with sea sand.

2.2. Apparatus

The PHWE–LC–GC apparatus is shown in Fig. 1. The PHWE system, which was self-constructed, consisted of an extraction unit with a solid-phase trap, a GC oven (HP 5790A, Agilent, Palo Alto, CA, USA), two Jasco PU-980 pumps (Tokyo, Japan) and a manually adjustable, needle valve type pressure restrictor (Jasco). A three-way valve (HIP 30-15 HF4-HT, High Pressure Equipment, Erie, PA, USA) was used for directing water, drying gas or solvent towards the trapping column. A special high-temperature vessel (Keystone Scientific, Bellefonte, PA, USA) was used in the extractions. Connections between pumps, valves, extraction vessel and restrictor were of 1/16 in. stainless steel tubing of 0.5 mm I.D. (1 in.=2.54 cm).

The solid-phase trapping column (5 cm×2.1 mm I.D.) was packed with Tenax TA (80–100 mesh) adsorbent (Alltech, Deerfield, IL, USA). In the inlet of the trapping column there was a stainless steel frit

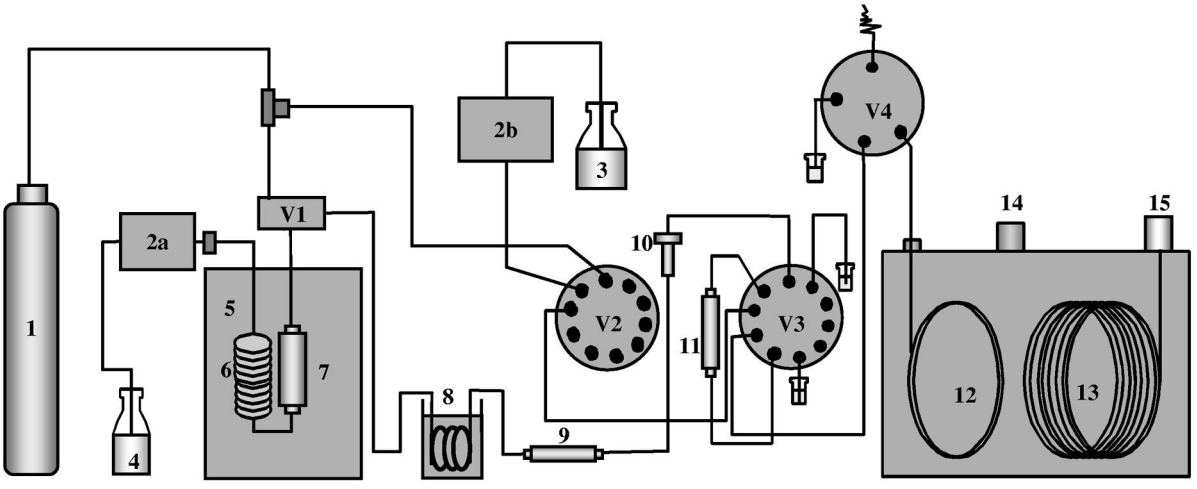

Fig. 1. PHWE–LC–GC apparatus. 1=N_2; 2a,2b=pumps; 3=elution and LC solvent; 4=water; 5=oven; 6=preheating coil; 7=extraction vessel; 8=cooling coil; 9=trapping column; 10=restrictor; 11=LC column; 12=precolumns; 13=analytical column; 14=SVE; 15=detector; V1=extraction valve; V2–V4=multiport valves.

with a pore size of 10 μm. The pore size of the frit in the column outlet was 2 μm.

The LC–GC system was a Fisons Instruments Dualchrom 3000 Series on-line high-performance liquid chromatography–high-resolution gas chromatography (Carlo Erba, Milan, Italy) containing a Phoenix 30CU pump. The LC column was a 15 cm×3.0 mm I.D. Luna cyano column (Phenomenex, Torrance, CA, USA) with a particle size of 5 μm. The eluent was pentane–ethyl acetate (85:15, v/v) at a flow-rate of 0.25 ml/min. In the GC system a 3 m×0.53 mm I.D. 1,2-diphenyl-1,1,3,3-tetramethyldisilazane (DPTMDS)-deactivated retention gap (BGB Analytik, Zurich, Switzerland) was connected to a 20 m×0.25 mm I.D. analytical column (HP-5, 0.25 μm phase thickness) and to a solvent vapour exit (SVE) via a glass pressfit Y-piece. Detection was by flame ionisation detection (FID) at 300°C, detector gases being air (150 kPa) and hydrogen (50 kPa). The carrier gas was helium at 150 kPa.

All the tubings connecting the extraction unit to the LC system and the LC system to the GC system were of stainless steel (0.5 mm I.D.), PEEK [poly-(ether ether ketone), 0.5 mm I.D.] or PTFE (0.5 mm I.D.). The extract was transferred from LC to GC via valve V4 and to the on-column injector via a fused-silica capillary (TSP100170, 100 μm I.D.×170 μm O.D.).

During the PHWE–LC–GC method development, three cyano columns were tested, Capcell CN S-5 (10 cm×2.1 mm I.D., 5 μm particle size, Capcell Pak, Shiseido, Tokyo, Japan), Spherisorb CN S-5 (10 cm×2.1 mm I.D., 5 μm particle size, Phase Separations, Deeside, UK) and Luna Phenomenex (15 cm×3.0 mm I.D., 5 μm particle size); two silica columns, Beckman Ultrasphere Si (10 cm×2.0 mm I.D., 5 μm particle size, Beckman Instruments, Berkeley, CA, USA) and Hypersil MOS (20 cm×4.6 mm I.D., 5 μm particle size, Shandon, Sewickley, USA); and an amino column, Asahipak NH_2P-50 (25 cm×2.1 mm I.D., 5 μm particle size, Asahi, Tokyo, Japan).

2.3. Analytical procedure

The analytical procedure can be divided into the four steps described below. During the extraction the analytes were trapped in the Tenax TA column and the water was directed to waste. The trapping column was dried with nitrogen for 20 min after each extraction. After drying of the extract it was eluted to the LC column with 3.5 ml of pentane–ethyl acetate (85:15, v/v) eluent mixture by switching of the valve V2.

2.3.1. Pressurised hot water extraction

The previously optimised extraction conditions for brominated flame retardants [11] were used in this study. At the beginning of the extraction the water flow-rate was adjusted to 1 ml/min (pump 2a in Fig. 1) and the pressure was adjusted to 118 bar using the needle valve type restrictor. Before the oven temperature was raised it was confirmed that there were no leaks in the system. The sample was extracted for 40 min at 325°C. After extraction, the water was cooled by passing it through a cooling capillary of stainless steel placed in a cold water bath. The analytes were then trapped in the Tenax TA column. The water flow was stopped by closing valve V1 and pump 2a after the extraction. The column was dried with nitrogen (8 bar) for 20 min to remove water before elution of the analyte fraction to the LC–GC system.

2.3.2. Transfer to LC and LC clean-up

The valve V2 was switched, and the pump 2b pushed the eluent (pentane–ethyl acetate, 85:15, v/v) through the trapping column and to the LC column with an eluent flow-rate of 0.25 ml/min. To protect the LC column the valve V3 was open for the first 3 min 50 s and directed the air coming from the extraction system to waste.

2.3.3. Transfer to GC

When the fraction containing the analytes had eluted from the LC column, valve V4 was switched and the fraction was transferred to the GC system via an on-column interface. The fraction volume (9 min 30 s to 14 min) was 1125 μl. During the transfer, fully concurrent solvent evaporation was applied at 80°C, with the SVE kept open. The SVE was closed 1 min 30 s after the transfer was complete and valve V4 was closed immediately when the transfer of the fraction containing the analytes was finished.

2.3.4. GC analysis

The oven was programmed from 80°C (8 min) to 180°C (2 min) at 15°C/min, from 180 to 260°C at 2°C/min and finally to 300°C (15 min) at 10°C/min.

After the transfer, the tubings attached to the extraction vessel and the trapping column were flushed with pentane–ethyl acetate (85:15, v/v) and then dried with a flow of nitrogen. The next extraction could then be started while the GC analysis of the previous extraction was still proceeding.

2.4. GC–MS for confirmation of analyte identification

Two GC–MS systems were used to confirm the identification of the analytes. In the first, 2 μl of a 25 μg/ml standard containing the brominated flame retardants in ethyl acetate was injected on-column to a GC–MS (Hewlett-Packard 5890 gas chromatograph, 5989A quadrupole mass spectrometer, Agilent) using the same temperature program as in LC–GC. The MS analysis was carried out in the scan mode with electron impact ionisation (EI, 70 eV). The temperature of the GC–MS interface was 300°C, that of the ion source 250°C and that of the analyser 120°C. The analytical column of the gas chromatograph was a 25.0 m×0.2 mm I.D. HP-5 column (Agilent) of 0.11 μm phase thickness. A 3.0 m retention gap (BGB Analytik) with 0.53 mm I.D. and DPTMDS deactivation was connected to the analytical column with a press fit connector (BGB Analytik). In the second system the GC–MS system consisted of a large-volume GC system (HRGC 5300, Carlo Erba) and an MS instrument (Automass Solo, Thermoquest, Argenteuil, France). In the GC system, a 10 m×0.53 mm I.D. DPTMDS-deactivated retention gap (BGB Analytik) and a 3 m×0.32 mm I.D. HP-5 retaining precolumn with 0.25 μm phase thickness were connected to a 20 m×0.25 mm I.D. HP-5 analytical column with 0.25 μm phase thickness and to an SVE. The injection volume was 500 μl. The temperature program was the same as in LC–GC. The temperature of the GC–MS interface was 300°C and that of the ion source 200°C. Analyte identification was also confirmed with the GC–FID system of the Dualchrom 3000 Series apparatus with a large-volume injection [1 ml of 0.05 μg/ml standard containing the brominated flame retardants in pentane–ethyl acetate (85:15, v/v) solution, injected from a loop made of stainless steel].

3. Results and discussion

The analysing system consisted of a PHWE unit connected on-line with LC–GC. A similar system was used earlier [18] for the analysis of sediment samples for PAH compounds. Different from the earlier system, in which the solid-phase trap also served as an LC column, in this study an extra LC column was added between the trap and the GC column. The aim in doing this was to achieve more efficient clean-up of the extract, because the concentration of brominated compounds in sediment samples was assumed to be lower than that of PAH compounds. The extra LC column also improved the fractionation and concentration of the extract. In our previous work, we used small sample amounts (10–50 mg) [18]. In this study, larger sample amounts allowed better sample homogeneity. The choice of the eluent played an important role in the optimisation of PHWE. For the method to be practical the elution solvent for the trap and the LC eluent should be the same. In addition, minimisation of the fraction to be transferred to the GC required consideration of the strength of the eluent. The fraction containing the analytes should be eluted as a narrow band from both the trap and the LC column. Another requirement for the eluent was that it should be compatible with GC.

3.1. Pressurised hot water extraction

In our earlier study [11], conditions for extracting BFRs from sediment with pressurised hot water were optimised (extraction time, extraction temperature, breakthrough, comparison to Soxhlet extraction, behaviour of the analytes). The optimised conditions were used in this study. For the developed on-line system, first the optimal trap material and volume were selected. In the beginning, we used a 2 cm×2.1 mm I.D. solid-phase trap packed with Tenax TA, 80–100 mesh. However, even with low concentrations it could not retain the analytes and breakthrough occurred. The breakthrough level was studied by extracting the water coming through the trap with isooctane. It was found that considerable

amounts of the analytes were not retained in the trap and were eluted with the water. The trap was subsequently changed to a longer one, 5 cm×2.1 mm I.D., packed with the same Tenax TA, 80–100 mesh. In addition, other materials were tested with the same trap volume (Tenax TA, 60–80 mesh and Tenax GR, 80–100 mesh). Tenax GR contained a large amount of impurities that disturbed the GC analysis. From among the tested solid-phase columns and materials, no breakthrough occurred with the 5 cm×2.1 mm I.D. column packed with Tenax TA and this combination was selected for further studies. The trap breakthrough can also depend on the temperature of the water entering the trap. In this case a cooling capillary in front of the trap ensured that the temperature of the water reaching the trap was near ambient. The measured temperature was 24.8°C. Pentane–ethyl acetate is known from previous work [11] to be an effective solvent mixture for eluting brominated compounds from the trap and it was also selected for further studies.

Because no certified sediment sample was available with known concentrations of the brominated analytes, the extraction efficiency of the PHWE was compared to Soxhlet extraction in the previous study [11]. The Soxhlet extraction gave extraction yields of less than 36% compared to the PHWE.

3.2. LC columns

Since the concentrations of other compounds (alkanes, PAHs) in sediments are typically much higher than those of BFRs, the BFRs must be separated from these other compounds. Otherwise, the GC column will be overloaded with the large volume introduction. The other compounds also disturb the GC separation. We sought, therefore, a normal-phase LC column on which to efficiently clean-up and concentrate the extract and to fractionate brominated compounds, alkanes and PAH compounds.

Silica, amino and cyano columns were investigated in a search for the best conditions for the LC separation. Also, different eluent mixtures were compared. Two cyano columns, Capcell CN S-5 and Spherisorb CN S-5, and then a silica column, Beckmann Ultrasphere Si, were studied, but none gave a satisfactory separation of alkanes, PAHs and brominated compounds. The eluent mixtures tested with these columns were pentane, ethyl acetate–pentane (15:85) and ethyl acetate–cyclohexane (15:85). Next, the Hypersil MOS column with pentane, pentane–ethyl acetate (85:15, v/v) and pentane–ethyl acetate (50:50, v/v) as eluents was studied, again without satisfactory results. Good separation was finally obtained with an Asahipak NH_2P-50 amino column and a Luna Phenomenex cyano column. The cyano column was chosen for further studies, with pentane–ethyl acetate (85:15, v/v) as eluent, and with this column brominated compounds, alkanes and PAHs could be separated from each other.

3.3. LC–GC transfer

An on-column interface with fully concurrent eluent evaporation was tested for the transfer of the fraction from LC to GC. Fully concurrent solvent evaporation (transfer temperature 80°C) was chosen because the analytes were relatively nonvolatile. A flow-rate of 0.25 ml/min was used during the transfer. Problems with back-flow of eluent vapours to the injector arose with the typical large-volume transfer column configuration (10 m×0.53 mm I.D. retention gap and 3 m×0.32 mm I.D. retaining precolumn) and a short, wide-bore retention gap (3 m×0.53 mm I.D.) was chosen instead.

In addition to the on-column interface we also tested the loop type interface, which was especially designed for fully concurrent solvent evaporation. However, problems were encountered in reaching satisfactory carrier gas flow-rates and the on-column interface was preferred. The transfer temperature was above the boiling point of pentane and the short retention gap allowed high carrier gas flow-rates. Using this configuration the eluent back-flow to the injector was avoided and the time required for the evaporation of the solvent was shortened and, therefore, also the analysis times.

The transfer efficiency from the LC column to the GC was evaluated by comparing large-volume injections of standards to GC and to LC–GC. The average recovery of the transfer from LC to GC was 96%.

3.4. Quantitative analysis

After optimisation of the PHWE–LC–GC conditions, the linearity of the method was studied with standards spiked into acid-washed sea sand in the concentration range 0.0125–10 μg (eight different concentrations, three replicates). A PHWE–LC–GC chromatogram of the spiked sea sand is shown in Fig. 2a. The method was linear from 0.0125 to 2.5 μg, the linearity being between 0.95 and 0.999 for all the compounds studied except PHT4. The linearity results are listed in Table 1. The total recovery of the whole PHWE–LC–GC system was 67.6%, on average. Breakthrough from the trap occurred with higher concentrations of analytes (5 and 10 μg). Thus, when samples contain high concentrations of analytes, the volume of the packing material of the solid-phase trap should be increased. The amounts of brominated flame retardants in sediment samples are typically low, however.

One analyte, tetrabromophthalic anhydride (PHT4), gave unrepeatable results. Three replicate ''bomb'' experiments were carried out to determine whether or not PHT4 decomposed during the extraction due to the high temperature. The PHT4 standard was placed in a vessel, which was then filled with water, and kept in an oven for 2 h at 325°C. The contents of the vessel were extracted with dichloromethane (3×2 ml) and the extract was dried with Na_2SO_4, filtered, concentrated and analysed by GC–MS. PHT4 was not detected in the GC–MS analysis. This would suggest that the ether bond was hydrolysed under the extraction conditions, as has been shown for diphenylether in supercritical water [20]. There was no evidence of decomposition with the other analytes.

Two different sediments, JML and 1529:1, were analysed with the developed PHWE–LC–GC method. The sample amount that was used was 100 mg. The results are summarised in Table 2. In sediment JML, tetrabromodichlorocyclohexane, pentabromochlorocyclohexane, hexabromobiphenyl (BP6) and heptabromobiphenyl were found in concentrations of 11.3–68.8 ng/g. Tris(2,3-dibromopropyl)phosphate (T23P) was found as well, but it could not be quantified because in the linearity studies it eluted together with tetrabromobisphenol A (BP4A). A PHWE–LC–GC chromatogram of sediment JML is shown in Fig. 2b. In sediment 1529:1, tetrabromodichlorocyclohexane, pentabromochlorocyclohexane and heptabromobiphenyl were found in concentrations of 37.75–126.47 ng/g. For all the samples the repeatability of the retention times was 0.04–0.18% and the repeatability of the peak areas 3.2–35.0%. The limits of detection ($S/N = 3$) were in the range 0.70–1.41 ng/g and the limits of quantification ($S/N = 10$) were 6.16–12.3 ng/g.

To confirm the identification of the peaks, the PHWE extract was collected after the LC clean-up, dried with Na_2SO_4, filtered and concentrated to 50 μl under nitrogen flow. The concentrated extract was analysed by GC–MS in the scan and selected ion monitoring (SIM) modes. GC–MS confirmed the identification of all peaks, and, in addition, tribromotrichlorocyclohexane was found in both sediments. Tribromotrichlorocyclohexane could not be identified with FID because of overlapping peaks. Compared with chromatograms obtained by off-line PHWE–GC [11], those obtained by PHWE–LC–GC are much cleaner. In addition, because the analysis in the PHWE–LC–GC system took place in a closed system, no sample losses occurred and the reliability of the analysis was improved.

Only technical mixtures of the brominated compounds were available as standards for this study. It is probable, therefore, that the mixtures contained compounds that did not elute from the GC column under the temperature program employed, causing the amounts of brominated flame retardants found in the sediments to be slightly too high. Also, some of the peaks may have contained several isomers that could not be separated from each other.

Compared to the earlier study (PHWE with off-line GC–MS) [11], slightly higher results for the BFRs were obtained, especially for the most volatile analytes. This is probably because, with the off-line system, the extract had to be concentrated by evaporation before the GC analysis, and therefore possible losses of these compounds occurred. With our closed PHWE–LC–GC system, there are no losses of volatile analytes under the optimised conditions.

4. Conclusions

The pressurised hot water extraction–liquid chro-

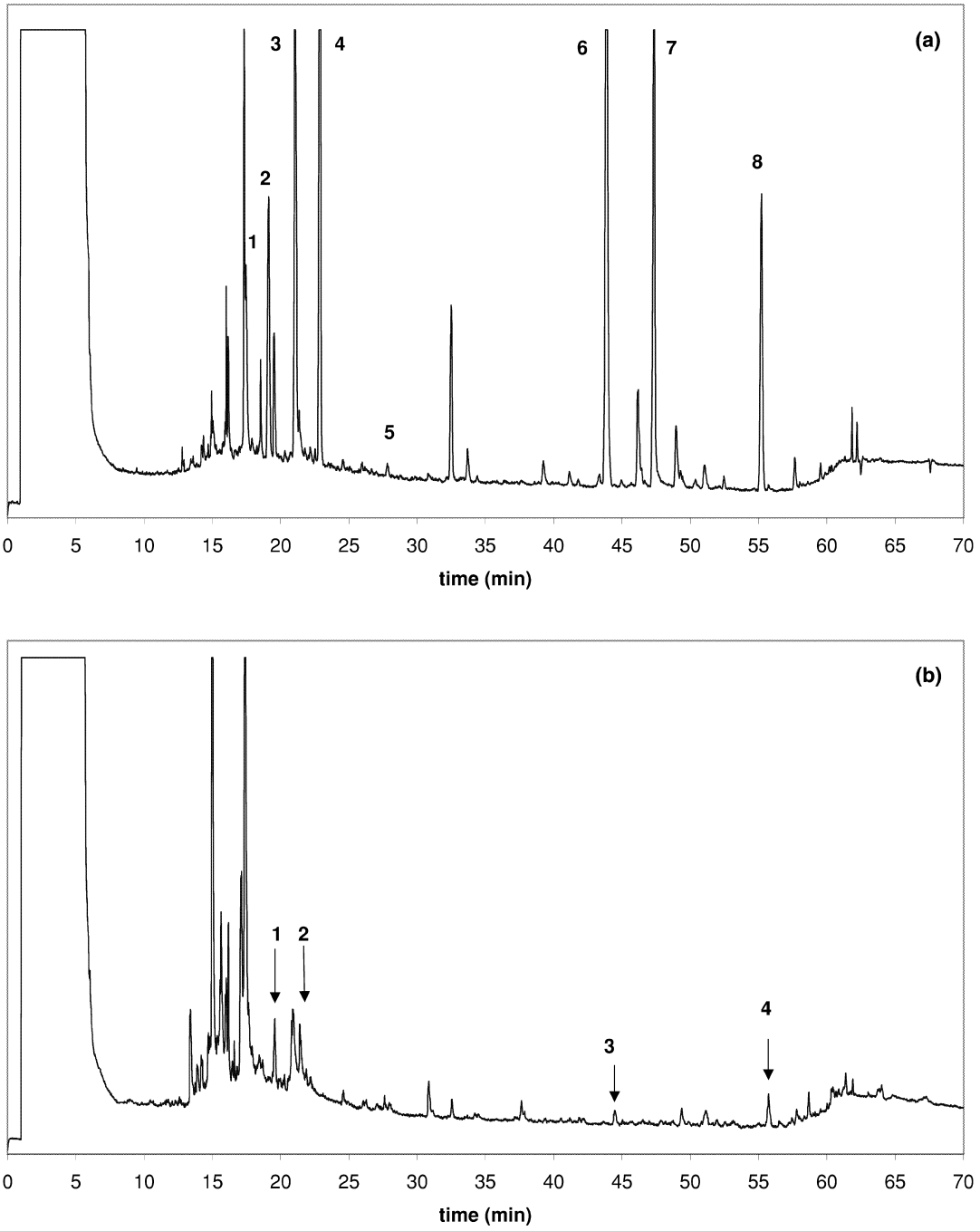

Fig. 2. (a) PHWE–LC–GC chromatogram of spiked sea sand. For analytical conditions, see text. Peak identification: 1 = tribromotrichlorocyclohexane, 2 = tetrabromodichlorocyclohexane, 3 = pentabromochlorocyclohexane, 4 = pentabromotoluene, 5 = PHT4, 6 = BP6, 7 = BP4A and T23P, 8 = heptabromobiphenyl. (b) PHWE–LC–GC chromatogram of sediment JML. For analytical conditions, see text. Peak identification: 1 = tetrabromodichlorocyclohexane, 2 = pentabromochlorocyclohexane, 3 = BP6, 4 = heptabromobiphenyl.

Table 1
Characterisation of the method for determination of brominated flame retardants in sediment: linearity shown as correlation coefficients, limits of detection (LOD) and quantification (LOQ), and repeatability of retention times (t_R) and peak areas for spiked sea sand ($n=3$). For analytical conditions, see text

Analyte	Linearity	LOD (ng/g)	LOQ (ng/g)	t_R (RSD, %)	Peak area (RSD, %)
Tetrabromodichloro-cyclohexane	0.9813[a]	1.41	12.3	0.17	13.0
Pentabromochloro-cyclohexane	0.9899[b]	1.41	12.3	0.14	10.9
Pentabromotoluene	0.9887	1.41	12.3	0.04	1.8
BP6	0.9938[c]	0.70	6.2	0.05	4.2
BP4A+T23P	0.9499	1.40	12.3	0.39	28.0
Heptabromobiphenyl	0.9984[d]	0.71	6.2	0.05	5.3

[a] Concentration range 0.004–0.83 μg.
[b] Concentration range 0.006–1.25 μg.
[c] Concentration range 0.009–1.88 μg.
[d] Concentration range 0.003–0.63 μg.

matography–gas chromatography method that was developed works well in the extraction and analysis of brominated flame retardants. The method provides very good sensitivity compared to traditional methods and the amount of sample can be drastically reduced as a result. The LC column works well in fractionation of the extracts, and clean extracts are obtained. One of the advantages of our on-line system is that the better sensitivity due to large volume injection to the GC allows MS in scan mode to be used for detection. The analyte identification then becomes more reliable. The new system is highly suited for samples in which the amounts of analytes are very low. And, even then, less sensitive detectors can be used. If the concentration of the analytes is very low, the sensitivity can be increased simply by increasing the sample amount. The method is so sensitive that even FID can be used as the detection method.

Table 2
Determination of brominated flame retardants in sediment samples JML (5–10 cm) and 1529:1 ($n=3$). For analytical conditions, see text

Analyte	1529:1 (ng/g)	JML (ng/g)
Tetrabromodichloro-cyclohexane	126.5±20.2	68.8±16.0
Pentabromochloro-cyclohexane	37.8±1.2	45.7±3.7
BP6	–	11.3±0.6
Heptabromobiphenyl	44.8±15.7	15.8±5.5

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