

Improved derivatization protocol for simultaneous determination of alkylphenol ethoxylates and brominated flame retardants followed by gas chromatography-mass spectrometry analyses

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ABSTRACT

An improved derivatization protocol for the simultaneous determination of alkylphenol ethoxylates and brominated flame retardants with heptafluorobutyric anhydride under triethylamine amine base was investigated. The derivatization reaction was completed in 30 min at 50 °C using hexane as solvent. Under these conditions, it was observed that alkylphenol ethoxylates and tetrabromobisphenol A were derivatized successfully in the presence of hexabromocyclododecane, lower congeners of polybrominated biphenyls and polybrominated diphenyl ethers. The improved protocol was applied to the recover of the analytes of interest from a simulated water sample after solid phase extraction. The recoveries achieved were above 60%. The limit of detection and limit of quantification ranged from 0.01–0.20 and 0.05–0.66 $\mu\text{g L}^{-1}$, respectively. The improved derivatization procedure was also successfully applied to determine trace amounts of these compounds in environmental water samples. The concentrations of the targeted analytes from the environmental samples were determined from limit of quantification. The levels of the targeted compounds in the environmental samples ranged from $\text{nd}-7.63 \pm 2.83 \mu\text{g L}^{-1}$.

Key words | alkylphenol ethoxylates, brominated flame retardants, gas chromatography-mass spectrometry, heptafluorobutyric anhydride derivatization, simultaneous determination

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INTRODUCTION

Alkylphenol ethoxylates (APEs) and brominated flame retardants (BFRs) are of anthropogenic compounds which are often referred to as endocrine disrupting compounds (EDCs) because they have been reported to interact with the oestrogen receptors (Stehmann & Schröder 2004). Studies have shown that APE metabolites are more toxic than their parent compounds, are persistent and accumulate in fatty tissues (Ying *et al.* 2002; Petrovic *et al.* 2003; Gatidou *et al.* 2007; Sibali *et al.* 2010). Despite their benefits for reducing fire-related injury and property damage, growing concern about BFRs has risen because of their occurrence and persistence, and they have been detected in the environment, biota and in humans (Alaee *et al.* 2001; Hyötyläinen & Hartonen 2002; Polder *et al.* 2008; Vetter *et al.* 2008; Yu *et al.* 2008; Odusanya *et al.* 2009; Segev *et al.* 2009; Olukunle *et al.* 2011).

Some of the most frequently used methods for the analysis of these groups of compounds include: direct analysis using liquid chromatography-mass spectrometry (LC-MS) (Petrovic *et al.* 2003), gas chromatography with electron capture detector (GC-ECD) (Odusanya *et al.* 2009), gas chromatography-mass spectrometry (GC-MS) (Azevedo *et al.* 2001; Olukunle *et al.* 2011), gas chromatography-high resolution mass spectrometry (GC-HRMS) (Alaee *et al.* 2001; Lacorte *et al.* 2010), or indirect analysis using derivatization techniques (Ding & Tzing 1998; Cathum & Sabik 2001; Hoai *et al.* 2003; Esperanza *et al.* 2004; Stehmann & Schröder 2004; Fiedler *et al.* 2007; Gatidou *et al.* 2007; Dirtu *et al.* 2008). Derivatization techniques have been used to determine low volatility polar compounds such as phenolic analytes since such compounds show low sensitivity and tailing in gas chromatographic analysis (Gatidou *et al.* 2007). For the group of compounds covered in the present study, acetylation has been chosen because of its quantitative

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reactions with various hydroxyl compounds in relatively moderate conditions. In our previous paper, heptafluorobutyric anhydride (HFBA) was used as the derivatizing agent for the determination of APEs and BFRs analytes in environmental samples (Chokwe *et al.* 2012). However, the procedure described in that paper used Na_2CO_3 with a derivatization time of 2 h. In another study, Dirtu *et al.* (2008) derivatized BPA, Tetrabromobisphenol A (TBBPA) and triclosan using PFPA aided by triethylamine (TEA) at 70°C for 30 min. In another study, NP and BPA were derivatized within 30 min at 60°C using TFAA (Stehmann & Schröder 2004). Derivatization of Nonylphenol Ethoxylate (NPEO) with *n*-propanol-acetylchloride at 80°C for 1 h has also been reported (Ding & Tzing 1998). Cathum & Sabik (2001) described a derivatization procedure for APnEO using pentafluorobenzoyl bromide (PFB-Br) as derivatizing agent aided with K_2CO_3 by sonication. The derivatization took 2 h and was conducted in the dark. Gatidou *et al.* (2007) reported derivatization of NP, NP2EO, BPA and triclosan with bistrimethylsilylfluoroacetamide (BSTFA) at 65°C for 20 min, while Fiedler *et al.* (2007) derivatized APs with the same reagent at room temperature for 2 h. Furthermore, NPnEO was derivatized with BSTFA in the presence of trimethylchlorosilane (TMCS) at 70°C for 4 h (Esperanza *et al.* 2004). In a separate study, Hoai *et al.* (2003) reported derivatized NPnEOs and NPnECs with bistrimethylsilylacetamide (BSA) at 25°C for 1 h.

In the aforementioned derivatization studies, either higher temperatures and shorter derivatization time, or lower temperatures and longer derivatization times in the presence of different bases were reported. It is essential that a balance between derivatization temperature and time should be determined since high temperatures and long derivatization times may not favour analytes of interest that are unstable, that is, BFRs, where debromination of higher congeners to lower congeners is possible. This study, therefore, reports on improved protocol using HFBA enhanced by triethylamine base derivatization using hexane as the solvent and followed by gas chromatography-mass spectrometry analysis, for the simultaneous determination of APEs and BFRs in environmental samples. The approach developed in the present study is seen to be milder (50°C), with a shorter derivatization time (30 min), and saves sample handling since these compounds can be analyzed simultaneously.

PREPARATION

Sample preparation plays an important role in the analysis of APEs and BFRs in environmental samples because

these analytes are present at trace levels. Typically these analytes are extracted from the samples, purified and concentrated before the final analysis.

CHEMICALS AND STANDARDS

Derivatizing agent HFBA was of analytical grade purchased from Sigma-Aldrich South Africa. The solvents methanol, dichloromethane, acetone and hexane used in the study were of GC grade and were used without further purification. The APEs and PBBs were purchased from Laboratories Dr Ehrenstorfer-Schäfers, Augsburg. Only the nonylphenol ethoxylates (NPE), nonylphenol penta ethoxylates (NPPE) and octylphenol penta ethoxylates (OPPE) were of technical grade and both the remaining APEs and polybromobiphenyls (PBBs) were of analytical grade. The polybrominated diphenyl ethers (PBDEs) mixtures were purchased from AccuStandard, USA, and were of analytical grade. TBBPA of technical grade (as Firemaster BP4A) and hexabromocyclododecane (HBCD) of technical grade were purchased from AccuStandard, USA. Helium (as He 5.5 pure) was purchased from Air Product South Africa, Vereeniging.

GC-MS analysis

An Agilent 6890 GC equipped with 5975 mass selective detector was used for GC-MS analysis. The MS was tuned with perfluorotributylamine using the auto-tune program. The GC was equipped with an Agilent autosampler. The GC separation was performed on a capillary column (Restek RT \times -1614, film thickness $0.10\ \mu\text{m}$, $15\ \text{m} \times 0.25\ \text{mm}$ I.D. (ChromSpec cc South Africa)). The GC-MS conditions used for analysis were as follows: carrier gas He; linear velocity, $40\ \text{cm s}^{-1}$; injector temperature, 280°C ; transfer line temperature, 300°C ; ion source 150°C . For analysis, $1\ \mu\text{L}$ splitless injections were carried out by autosampler. The GC temperature program conditions were as follows: initial temperature 50°C ; heated to 120°C by a temperature ramp of $7.5^\circ\text{C min}^{-1}$, then 275°C by a temperature ramp of $15^\circ\text{C min}^{-1}$, then finally heated to 300°C (held for 2 min) by a temperature ramp of $25^\circ\text{C min}^{-1}$.

Derivatization

Into a Pyrex test tube, $80\ \mu\text{L}$ of organic mixture containing APs ($1\ \text{mg L}^{-1}$), APEs ($5\ \text{mg L}^{-1}$), PBBs ($1\ \text{mg L}^{-1}$), PBDEs ($1\ \text{mg L}^{-1}$), HBCD ($5\ \text{mg L}^{-1}$) and TBBPA ($5\ \text{mg L}^{-1}$),

0.1 ml hexane; 70 μL of 0.1 M TEA and 7 μL HFBA was added. The test tubes were closed and completely mixed for 1 min using a vortex system. The contents were gradually heated to 50 $^{\circ}\text{C}$ and the derivatization monitored by GC-MS. Derivatization was achieved within 30 min. Thereafter, the contents were cooled, quenched with 0.3 mL of 5% aqueous solution of K_2CO_3 . The organic phase was then drawn off. The aqueous phase was washed twice with 0.5 mL of hexane to recover organic fractions. After separation, the organic phase extracts were concentrated to 100 μL . Thereafter, the internal standards (Chrysene and PBB80) were added into the extract, the volume made up to 200 μL and 1 μL of a mixture of extracts and internal standards injected into the GC-MS.

Extraction of analytes from simulated water sample

Solid-phase extraction (SPE) was used as the isolation technique throughout the experiment. Before use, the SPE

cartridge was conditioned with 6 mL of 30% MeOH in DCM followed by the addition of 6 mL of MeOH. About 250 mL of MilliQ water, spiked with 80 μL of organic mixture, was acidified to pH 3 with acetic acid and extracted at a flow rate of approximately 10 mL min^{-1} . After passing the sample, the cartridge was dried under vacuum for 1 h. The compounds were eluted with 3 \times 2 mL of mixture of DCM-hexane (4:1). The eluates were evaporated to dryness under a gentle stream of nitrogen at 40 $^{\circ}\text{C}$. Finally the dried residues were subjected to derivatization reaction as described earlier.

WATER SAMPLE COLLECTION

Environmental water samples were collected from three sites, A, B and C, along the Grootdraai sub-catchment located in the Mpumalanga Province, South Africa, as shown in Figure 1. The sub-catchment is supplied by tributaries from Blekbokspruit and the Brummerspruit. Key

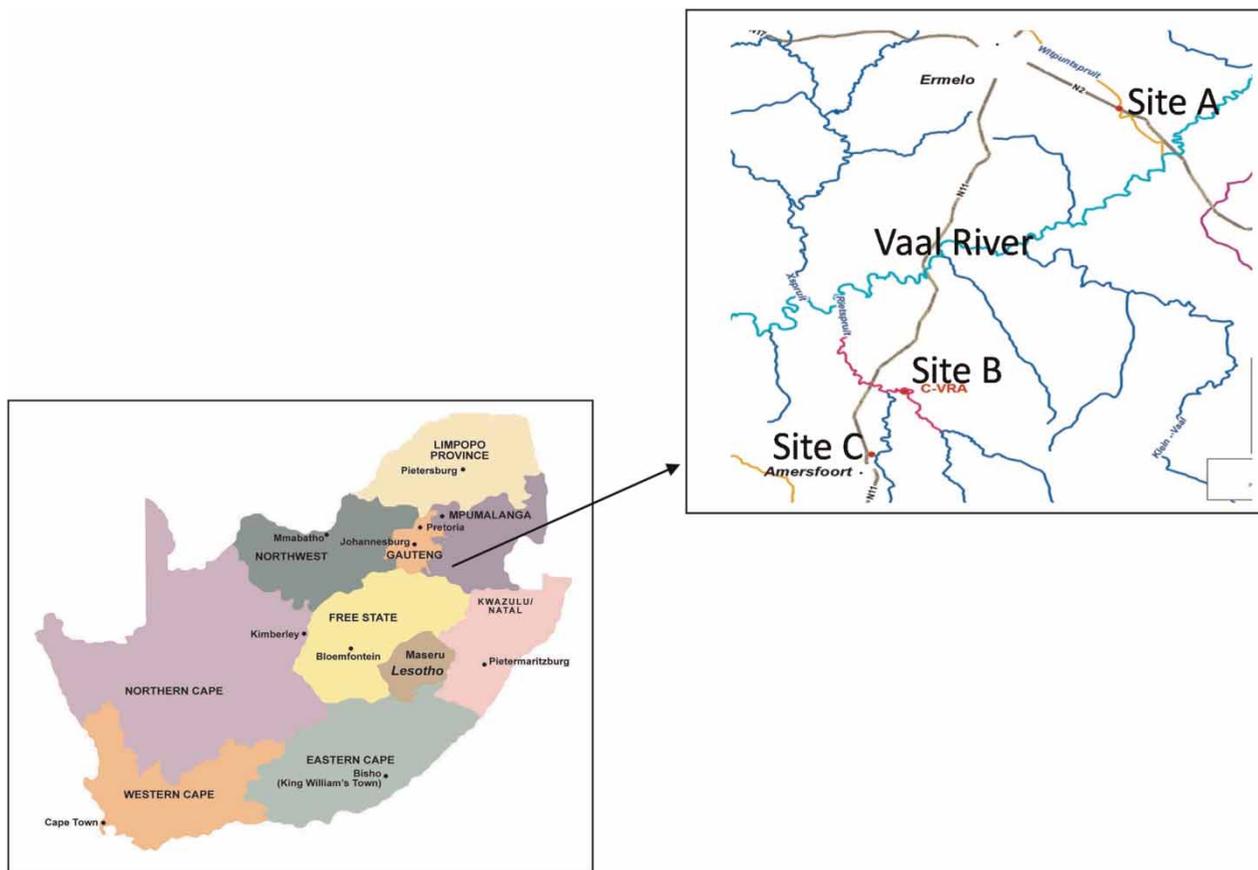


Figure 1 | Map of Grootdraai sub-catchment area.

activities in the sub-catchment include flows from wastewater treatment works (WWTW), stock farming, irrigation agricultural activities, as well as the overall increase in human population around the sub-catchment area. Water samples were collected using 250 mL Winchester brown bottles by immersing a sample bottle below the surface and allowing it to fill. The samples were placed in cooler bags, transported to the laboratory and stored in a cold room set at a temperature of 4 °C until analysis. The samples were allowed to equilibrate at room temperature before use.

Extraction of analytes from environmental water sample

The collected samples were subjected to the extraction and derivatization procedures described above.

Quality assurance

The spiking method was used in the quality assurance process of analytical method due to the unavailability of certified reference material for the target compounds. MilliQ pure water was spiked with 80 µL of standard mixture of 1.0 mg L⁻¹ APs, PBBs and PBDEs; 5.0 mg L⁻¹ HBCD, TBBPA and APEs, and was taken through the same extraction and derivatization procedure mentioned above prior to GC analysis. Several quality assurance

measures were also routinely used in this study, including running blanks in between samples as well as analysing samples in triplicate.

RESULTS AND DISCUSSION

Derivatization

Heptafluorobutyric anhydride was chosen for the present study because of its rapid and quantitative reaction, the formation of stable products, excellent chromatographic properties for the targeted analytes as well as the availability of the reagent. The derivatization reaction was monitored by GC-MS using TBBPA as shown in Figure 2.

Both APEs and TBBPA were fully derivatized with HFBA aided by TEA in the presence of PBBs, PBDEs and HBCD. Under the scope of the derivatization, it was observed that there was no de-bromination of PBBs, PBDEs and HBCD. The GC-MS chromatogram, shown in Figure 3, indicates that only the hydroxyl groups reacted and this was later used to determine the selected ion monitoring of the target compounds; Table 1 shows the specific fragment ion to be used for quantification of the analytes from environmental samples. It was also observed that derivatization depended on the analyte structure, time and solvent. In this study, the derivatization reaction for the phenolic hydroxyl group was completed faster than those for

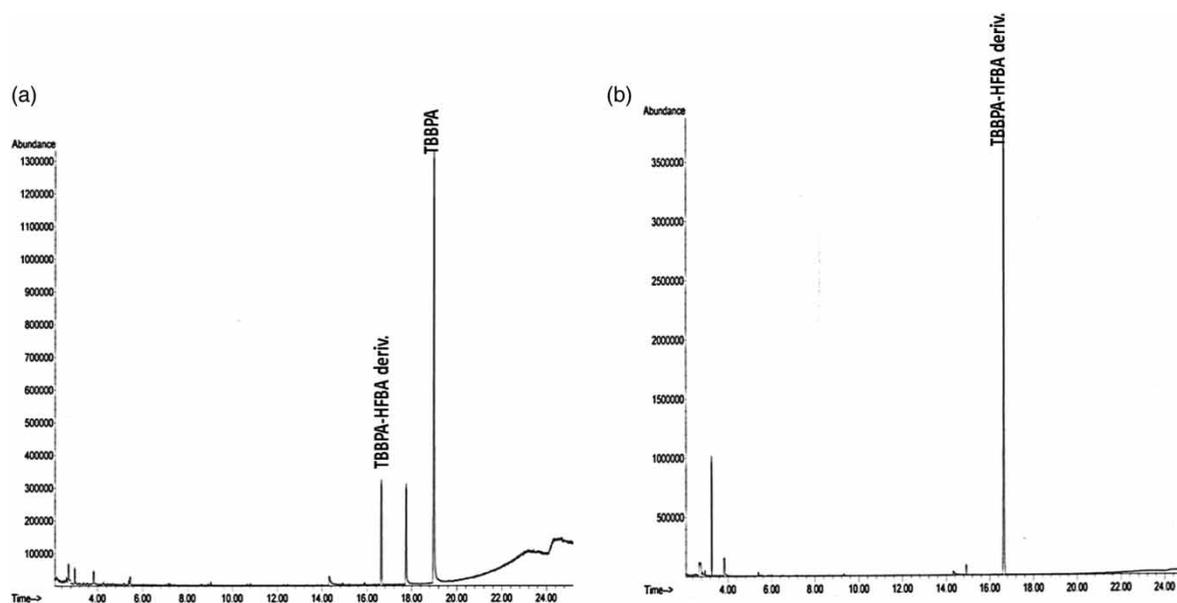


Figure 2 | GC chromatogram of TBBPA derivatized after (a) 10 min and (b) 30 min at 50 °C.

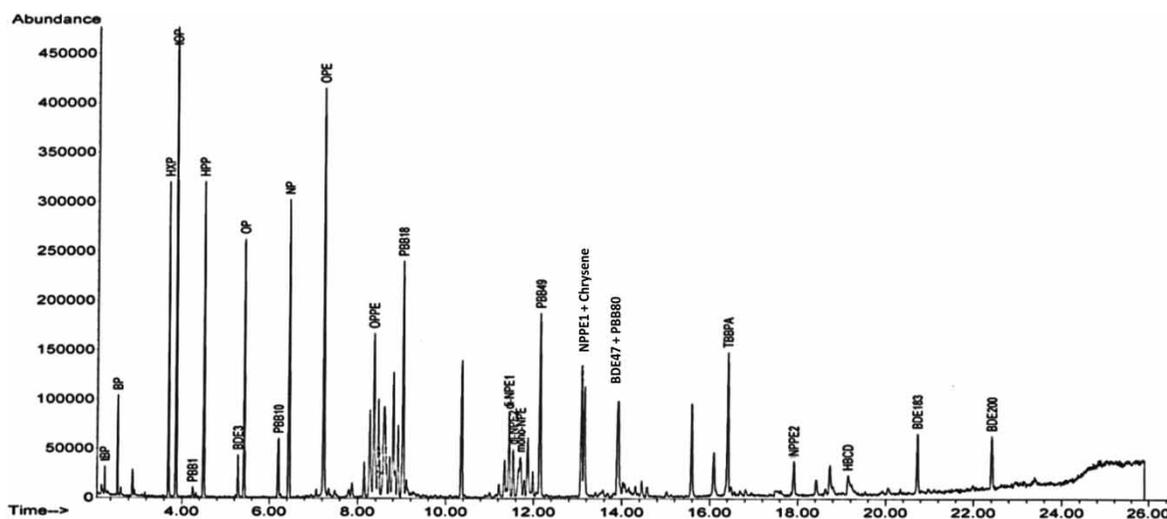


Figure 3 | GC chromatogram of derivatized APEs and TBBPA in the presence of PBBs, PBDEs and HBCD standard.

Table 1 | Specific fragment ions for the heptafluorobutyric derivatives

Compound	Fragment ions <i>m/z</i>
<i>t</i> -BP	331.1; 303
<i>n</i> -BP	303.1; 345
HXP	303.1; 374.2
<i>t</i> -OP	331
HPP	302.90; 387.9
OP	303.1; 402.1
NP	302.9; 416.1
OPE	375.1
OPPE	389.1; 375.1; 361.1; 431.1
di-NPE2	433.1; 419.1; 405.1; 475.1
di-NPE1	419.1; 433.2; 405.1; 475.4
mono-NPE	433.1; 461.1
NPPE1	463.2; 477; 519; 639
NPPE2	551.1; 565.1; 607.2; 639
PBB1	232
PBB10	311.9
PBB18	310.9; 232; 389.8
PBB-49	309.9; 469.7; 388.8
BDE3	248
BDE15	327.9
BDE-47	485.7; 325.9
TBBPA	724; 739
HBCD	239.1; 560.8
BDE183	561.7; 723.6
BDE-200	465.7; 704.6; 785.6; 625.6

the alcoholic hydroxyl groups. This phenomenon has been reported (Hoai *et al.* 2003).

Recovery of targeted analytes from simulated water sample

The recovery results from simulated water samples as shown in Figure 4 ranged from 60–140%. These results were comparable with those reported by other researchers (Cathum & Sabik 2001; Cai *et al.* 2005; Hoai *et al.* 2003; Gatidou *et al.* 2007; Dirtu *et al.* 2008). The obtained recovery results were considered to be satisfactory considering that different types of analytes with different chemical structure and polarities were extracted simultaneously.

Comparison of the derivatization protocol with other reported studies

A comparison of the derivatization procedure from this study and previous reported procedures is presented in Table 2, from which it can be seen that BSTFA yielded a fast derivatization reaction as the reaction was complete within 20 min., but this was obtained at a higher temperature (65 °C) (Gatidou *et al.* 2007). Another study by Fiedler *et al.* (2007) also used BSTFA but the reaction was done at room temperature for 2 h. These two studies indicate the effect of temperature for the derivatization with BSTFA as the derivatization was quicker at an elevated temperature than at room temperature. Hoai *et al.* (2003) obtained quicker derivatization products at room temperature with BSA than with BSTFA as the

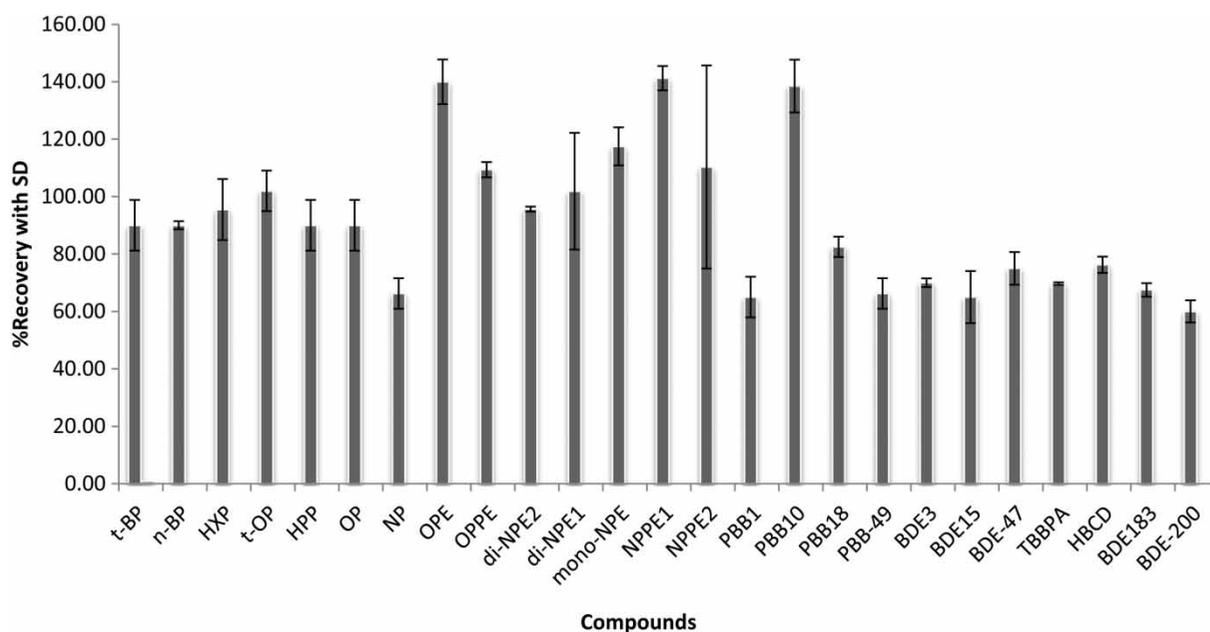


Figure 4 | Mean recoveries (%) of targeted compounds under optimum conditions.

Table 2 | Summary of derivatization procedures in water samples in the literature

Compounds	Derivatizing agent	Conditions	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Ref.
NPEO	<i>n</i> -propanol-acetylchloride	80 °C, 1 h 2 h ultrasonic bath then	NR	0.01	Ding & Tzing (1998)
APnEO	PFB-Br + K_2CO_3	Overnight in dark place	0.001–0.002	NR	Cathum & Sabik (2001)
NPnEOs, NPnECs	BSA	25 °C, 1 h	0.0025–0.018	NR	Hoai <i>et al.</i> (2003)
NP, BPA	TFAA	60 °C, 30 min	NR	NR	Stehmann & Schröder (2004)
NPnEO	BSTFA and TMCS	70 °C, 4 h	NR	NR	Esperanza <i>et al.</i> (2004)
NP, NP2EO, BPA, TCS	BSTFA	65 °C, 20 min	0.03–0.41	0.11–1.34	Gatidou <i>et al.</i> (2007)
AP	BSTFA	Room temperature, 2 h	NR	NR	Fiedler <i>et al.</i> (2007)
BPA, TCS, TBBPA	PFPA + TEA	70 °C, 30 min	0.02–0.04	0.05–0.280	Dirtu <i>et al.</i> (2008)
APs, APEs, TBBPA	HFBA + Na_2CO_3	55 °C, 2 h	0.01–0.15	0.05–0.66	Chokwe <i>et al.</i> (2012)
APs, APEs, TBBPA	HFBA + TEA	50 °C, 30 min	0.01–0.15	0.05–0.66	This study

NR = not reported; LOD = limit of detection; LOQ = limit of quantification.

derivatized products were obtained in 1 h. In terms of the speed of derivatization, this study showed a quicker derivatization reaction than all the others, except for the studies done by Gatidou *et al.* (2007). With acylation reagents, this study showed similar reaction times compared to the studies where anhydride derivatizing agent were used (Stehmann & Schröder 2004; Dirtu *et al.* 2008). Compared to the conditions reported in Table 3, the derivatization method from this study was found to save analysis time as the derivatization was complete

within 30 min under very mild condition, producing comparable LOD and LOQ results.

LEVELS OF APES AND BFRS IN THE ENVIRONMENTAL SAMPLES

The concentrations of the targeted analytes (analyzed in triplicate) from the environmental samples, as shown in Table 3,

Table 3 | Environmental levels of APEs and BFRs ($n = 3$)

Compound	Site A $\mu\text{g L}^{-1}$	Site B $\mu\text{g L}^{-1}$	Site C $\mu\text{g L}^{-1}$
<i>t</i> BP	ND	ND	ND
BP	ND	ND	ND
HXP	ND	ND	ND
<i>t</i> OP	ND	ND	0.07
HPP	ND	ND	ND
OP	ND	ND	ND
NP	ND	ND	ND
OPE	ND	ND	ND
OPPE	ND	ND	0.71
di-NPE1	ND	ND	ND
di-NPE2	ND	0.38	0.49
mono-NPE	ND	ND	0.60
NPPE1	ND	ND	ND
NPPE2	ND	ND	ND
PBB1	ND	ND	ND
PBB10	ND	ND	ND
PBB18	ND	ND	ND
PBB49	ND	ND	ND
BDE3	ND	ND	ND
BDE15	ND	ND	ND
BDE47	ND	ND	ND
TBBPA	ND	ND	ND
HBCD	3.23	7.38	7.63
BDE183	ND	ND	ND
BDE200	ND	ND	ND

ND = not detected.

were determined from LOQ. The results from environmental samples mainly indicated the presence of HBCD, as it was detected from all the sampling points, while one di-ethoxylate was detected from both the final effluent from sites B and C. Also from site C, *t*-OP ($0.07 \mu\text{g L}^{-1}$), OPPE ($0.71 \mu\text{g L}^{-1}$) and mono-NPE ($0.60 \mu\text{g L}^{-1}$) were detected. Gatidou *et al.* (2007) obtained similar results for mono-NPE ($0.56 \mu\text{g L}^{-1}$) from effluent from the WWTW of Mytilene City in Greece.

CONCLUSIONS

The derivatization method presented for the simultaneous determination of APEs and TBBPA gave comparable results to other derivatization studied in the literature. The

derivatization procedure in this study involved the reaction of these compounds, simultaneously in the presence of lower congeners of PBBs, PBDEs and HBCD, with HFBA under triethylamine base at 50°C for 30 min. The results of this study demonstrate that the presented method has acceptable relative recoveries of 60 ± 3.86 to 141 ± 4.24 for the target compounds, and adequate LOD and LOQ that ranged from $0.01\text{--}0.20 \mu\text{g L}^{-1}$ and $0.05\text{--}0.66 \mu\text{g L}^{-1}$, respectively. When the conditions developed were optimized and applied to environmental samples, most of the analytes were not detected with the exception of HBCD, which was detected from all the sites, and mono-NPE, di-NPE2, OPPE and *t*-OP detected only at site C. The presented method showed milder derivatization condition and shorter analysis time.

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