HEPTAFLUOROBUTYRIC ANHYDRIDE DERIVATIZATION OF ALKYLPHENOL ETHOXYLATES AND BROMINATED FLAME RETARDANTS FOR SIMULTANEOUS GC-MS DETERMINATION

Chokwe TB[1], Okonkwo OJ[2*], Sibali LL[3], Ncube EJ[1]

[1]Scientific Services, Rand Water, 2 Barrage Road, Vereeniging, 1930, South Africa; [2]Department of Environmental, Water and Earth Sciences, and [3]Directorate of Research and Innovation, Tshwane University of Technology, Nelson Mandela Drive, Pretoria, 0001, South Africa
OkonkwoOJ@tut.ac.za

INTRODUCTION

A number of recent studies have indicated the widespread occurrence of several organic compounds in wastewater and sewage sludge[1-6]. Among these compounds, alkyl phenol ethoxylates (APEs) and brominated flame retardants (BFRs) present a significant research interest due to their extended use in several consumer and personal-care products and their toxicological and physiochemical properties[2].

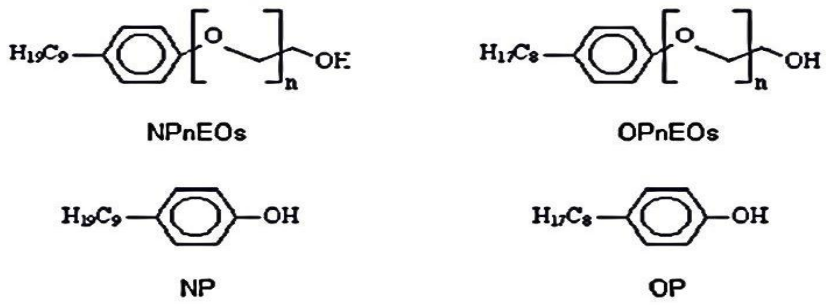

Figure 1: Structures of common APEs (nonyl- and octyl- phenol ethoxylates) and their metabolites

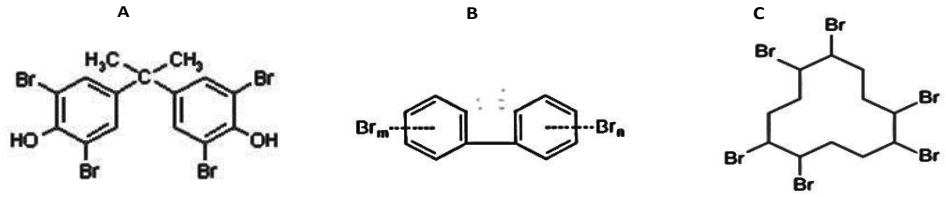

Figure 2: Structure of (A) TBBPA; (B) PBBs and (C) HBCD

Biodegradation of APE during wastewater treatment results in the production of more persistent and estrogenic metabolites, short chain APEs and alkyl phenols (APs) including nonyl phenol, octyl phenol. These metabolites are more toxic than the parent substances and they possess the ability to mimic natural hormones by interacting with the estrogen receptor[4]. However, information on levels on these compounds in any South Africa rivers is still scarce.

This study, therefore, reports on a simple and reliable procedure, based on SPE followed by HFBA derivatization and gas chromatography-mass spectrometry, for the simultaneous determination of APEs and BFRs in influent and effluent environmental samples obtained from a wastewater treatment plant.The approach adopted in the present study is seen to save analyses time and sample handling. Also the impact of filtration of samples on the recoveries of these compounds in real samples was investigated.

MATERIALS AND METHODS

MATERIALS

Standards and Reagents

Derivatizing agents (heptafluorobutyric anhydride (HFBA) was of analytical grade purchased from Sigma-Aldrich, South Africa. The solvents 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, Germany. Only the NPE, NPPE and OPPE were of technical grade and the remaining APEs and PBBs were of analytical grade. Tetrabromobisphenol A of technical grade as Firemaster BP4A and hexabromo cyclododecane of technical grade were purchased from AccuStandard, USA. Helium as He 5.5 pure was purchased from Air Product South Africa, Vereeniging.

Wastewater sample collection

Environmental water samples were collected from the Leeuwkuil wastewater treatment plant located in the Vereeniging region, South Africa. Water samples were collected at the inlet (influent) and at outlet (effluent) using Winchester 250 mL brown bottle. The samples were acidified and placed in cooler bags, transported to the laboratory and stored in cold room set at a temperature of 4°C. The samples were allowed to equilibrate at room temperature before use.

METHODS

Derivatization using HFBA

Into a vial, APs (1 mg L^{-1}), APEs (4 mg L^{-1}), PBBs (1 mg L^{-1}), HBCD (2 mg L^{-1}) and TBBPA (4 mg L^{-1}), 1 mL hexane; 10.5 mg Na_2CO_3 and 75 µL HFBA were added and the content heated to 55°C for approximately 1 h. Thereafter, the contents were cooled and the carbonate quenched with water. The organic phase was then drawn off and the volume made up to 1 mL. Thereafter, 1 µL was injected into the gas chromatography-mass spectroscopy analysis.

Instrumentation and GC/MS Conditions

An Agilent 6890 GC equipped with 5973 mass selective detector (MSD) was used for GC/MS analysis. The GC was equipped with a Gerstel autosampler. The GC separation was performed on a capillary column (Restek RTx-1614, film thickness 0.10µm, 15m x 0.25mm I.D., (Chromspec cc South Africa)). The GC/MS conditions used for analysis were as follows: carrier gas He; linear velocity, 40 cm s^{-1}; injector temperature, 275 °C; transfer line temperature, 280 °C; ion source 150 °C. For analysis 1µL splitless injection 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 °C/min then 275 °C by a temperature ramp of 15 °C/min then finally heated to 280 °C (held for 1 min) by a temperature ramp of 25°C min^{-1}.

Extraction of analytes in simulated water sample

About 250 mL of MilliQ water acidified to pH 3 with acetic acid was spiked with APs (1 mg L^{-1}), APEs (4 mg L^{-1}), PBBs (1 mg L^{-1}), HBCD (2 mg L^{-1}) and TBBPA (4 mg L^{-1}) were extracted using SPE cartridge (Strata C_{18}). Before use, the SPE cartridge was conditioned with 6 mL of 30% MeOH in DCM followed by the addition of 6 mL of MeOH at a flow rate of approximately 10 mL min^{-1} and the compounds eluted with 3 x 2 mL of mixture of DCM-Hexane. Thereafter, elutes were collected and reduced to dryness under gentle stream of nitrogen at room temperature. About 1 mL hexane; 10.5 mg Na_2CO_3, 75 µL HFBA were added and the content heated to 55 °C for approximately 1 h. Thereafter, the contents were cooled and the carbonate quenched with water. The organic phase was then drawn off and the volume made up to 1 mL with hexane. 1.0 µL of the derivatized sample was injected into the GC-MS.

RESULTS AND DISCUSSION

The optimized SPE extraction was then applied to environmental wastewater samples and the analytes were detected at low levels with the exception of nonylphenol penta ethoxylates (NPPE2) which gave inexplicable high concentration value (Table 1). When the influent was filtered before SPE extraction, though the extraction was much faster, the results showed that there are analytes losses during filtration because the analytes concentration were lower than when the influent was not filtered. This phenomenon was also observed by Sibali *et al*[1].

Table 1 Concentrations of APEs and BFRs in wastewater samples

Corrected Data Compound	Effluent µg L^{-1}	Influent µg L^{-1}	Influent Raw µg L^{-1}
t-BP	0.015	0.033	0.095
n-BP	0.033	0.200	0.200
HXP	ND	ND	ND
t-OP	0.038	0.036	0.105
PBB-1	ND	ND	ND
HPP	ND	ND	ND
OP	ND	ND	ND
PBB-10	ND	ND	ND
NP	ND	ND	ND
OPE	0.033	0.036	0.092
OPPE	1.461	4.566	4.259
PBB-18	0.014	0.015	0.018
PBB-49	0.014	0.016	0.018
di-NPE2	0.052	0.053	6.474
di-NPE1	0.550	10.615	10.268
mono-NPE	2.092	3.014	16.373
NPPE1	0.972	5.553	15.156

TBBPA	3.269	6.629	6.806
NPPE2	3.126	21.971	13.449
HBCD	0.142	0.1400	0.139

Effluent= final water leaving the plant; Influent= raw water filtered then acidified and MeOH added; Influent Raw = raw water acidified and MeOH added then filtered; ND = not detected.

ACKNOWLEDGEMENT

The authors are indebted to Rand Water for providing the technical environment and funding for this project which is part of Mr. Chokwe's doctoral degree, Mr. Carl Schoeman for fruitful discussions and Tshwane University of Technology for support.

REFERENCES

1. Sibali LL, Okonkwo JO, McCrindle RI. (2010) *Water SA* 36(3): 229-238
2. Gatidou G, Thomaidis NS, Stasinakis AS, Lekkas TD. (2007) *J. of Chromatogr. A* 1138: 32-41
3. Hoai PM, S. Tsunoi S, Ike M, Kuratani Y, Kudou K, Viet PH, Fujita M, Tanaka M. (2003) *J of Chromatogr. A* 1020: 161-171
4. Ying GG, Williams B, Kookana R. (2002) *Environ. Int*. 28: 215-226
5. Covaci A, Voorspoels S, Ramos L, Neels H, Blust R. (2007) *J of Chromatogr. A* 1153: 145-171
6. Vetter W, von der Recke R, Symons R, Pyecroft S. (2008) *Rapid Commun. Mass Spectrom.* 22: 4165-4170