Brominated Flame Retardants in Marine Mammals

SpeedExtractor E-916, Syncore® Analyst:
Extraction of Alternative Brominated Flame Retardants from Harbour Porpoises (Phocoena phocoena)

In recent years, the most widely used brominated flame retardants (BFRs), have been substituted with other, non-PBDE, BFRs. In this short note, a method for the analysis of aBFRs in biota samples is described. The method utilises pressurized solvent extraction with SpeedExtractor E-916 and concentration using a Syncore®, followed by a clean-up and analytics by GC-MS/MS. The recoveries of the aBFR in spiked samples were mostly between 70-120%. The monitored concentrations in marine mammals are generally low.

1. Introduction

The removal of the PBDEs from markets has resulted in a need for their substitution with other, non-PBDE, BFRs. There are a range of these 'alternative' BFRs (aBFRs) reported to be in use. Blubber from harbour porpoises collected as part of the UK Cetacean Strandings Investigation Programme (CSIP) were analysed using this method, in order to investigate the occurrence of aBFRs in the UK marine environment [1].

2. Experimental

Equipment: SpeedExtractor E-916, Syncore® Analyst

Samples: Twenty-one porpoise blubber samples were obtained from selected dead animals which were found stranded, or were by caught around the UK's coast. Tissue samples were stored frozen at −20 °C prior to analysis.

For quality control and method development, a spiked in-house laboratory sample (cod liver) was used.

Determination: Approx. 5 g of the sample was mixed with diatomaceous earth and sodium sulphate and extracted using the parameters in Table 1.

Table 1: Extraction parameters for SpeedExtractor E-916.

Parameter	Value
Temperature	100 °C
Pressure	120 bar
Solvent	Hexane 50 % : Acetone 50 %
Cell	40 mL
Vial	220 mL
No. of Cycles	3
Heat-up	1 min
Hold	5 min
Discharge	3 min
Flush with solvent	2 min
Flush with gas	3 min
Total extraction time	49 min

The samples were concentrated using a Syncore® Analyst and then cleaned-up with gel permeation chromatography (GPC) with ethyl acetate: cyclohexane 1:1 as mobile phase. The extracts were further cleaned-up on SPE-Florisil cartridges and the analytes were eluted with hexane and dichloromethane. The analysis was undertaken by gas chromatography - tandem mass spectrometry (GC-MS/MS) using electron ionization mode (EI).

3. Results

Recoveries for most alternative BFR compounds and BDEs in the cod liver reference materials using the full method were in the range 70–120%., see Table 2.

Table 2: Determined recoveries of aBFR in cod liver spiked at medium level (n=6, RSD % are in brackets).

ATE	52.3 (18.3%)	**HBB**	78.1 (10.6%)
α-TBECH	75.3 (8.9%)	**PBBB**	65.1 (12.9%)
β-TBECH	79.1 (9.0%)	**PBBA**	42.8 (34.2%)
BATE	79.4 (7.5%)	**HCDBCO**	85.4 (10.6%)
pTBX	78.3 (8.2%)	**EHTBB**	46.0 (22.6%)
β-TBCO	92.1 (5.4%)	**BB153**	95.9 (9.2%)
γ-TBECH	99.0 (5.1%)	**diMeTBBPA**	85.7 (35.4%)
δ-TBECH	103 (6.8%)	**BTBPE**	44.4 (48.7%)
TBoCT	76.8 (5.5%)	**TBPH**	41.7 (50.0%)
PBCC	65.0 (6.8%)	**s-DP**	80.7 (14.9%)
PBT	56.8 (11.2%)	**a-DP**	89.4 (14.9%)
PBEB	224 (45.6%)	**OBIND**	122 (15.3%)
DPTE	74.9 (10.4%)	**DBDPE**	133 (13.1%)

Concentrations of aBFR in harbour porpoise samples were in general low. Of the 30 individual compounds determined, 19 were not present and of the remaining 11 compounds, some were detected under the limit of quantification (*data shown in the Application Note*).

4. Conclusion

The extraction of aBFR from the spiked samples gave good recoveries, and the determination of these compounds in the porpoise samples gave low aBFR concentrations.

The presented screening method for the determination of aBFRs using SpeedExtractor E-916 for extraction and Syncore® Analyst for concentration is a powerful tool for monitoring the aBFR in the environment.

5. Acknowledgments

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6. References

[1] Law R.J., Losada S., Barber J.L, Bersuder P., Deaville R., Brownlow A., Penrose R., Jepson P.D. "Alternative flame retardants, Dechlorane Plus and BDEs in the blubber of harbour porpoises (*Phocoena phocoena*) stranded or bycaught in the UK during 2008", Environ.Int. 2013, 60: 81–88

For more detailed information please refer to the Application Note no. 206/2015.