COMPREHENSIVE ANALYTICAL APROACH FOR ORGANO-BROMINE COMPOUNDS IN ENVIRONMENTAL SAMPLES WITH GC-(NCI/EI)-LR/HRMS

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Introduction

Recently, environmental problems relating to brominated flame retardants (BFRs) have become a matter of great concern due to their potential toxic risk on human and wildlife [1] and recent increase in levels of polybrominateddiphenyl ethers (PBDEs)[2-4], in contrast to that of chlorinated organic compounds such as PCDDs/DFs and PCBs. Moreover, results on BFRs other than PBDEs, e.g., tetrabromobisphenol A (TBBPA) tribromophenol (TBP) and and hexabromocyclododecane (HBCD) are very much limited[5]. However, information about concentrations of BFRs in biological samples is scarcely available under the present circumstances in Japan. Consequently, it remains necessary to investigate the extent of pollution by and accumulation of these compounds. In this study, we report development of comprehensive analytical methodology for organo-bromine compounds in environmental sample with GC-(NCI/EI)-LR/HRMS and our findings regarding the concentrations of BFR and it's metabolite in a blubber of finless porpoise sample, in which intercalibration study on organobromine compounds was conducted in 2004[6].

Materials and Methods

Target compounds: We selected BFRs such as PBDEs, hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and TBBPA dimethyl ether metabolite of TBBPA, tribromophenol (TBP) and tribromo anisole metabolite of TBP. Additionally new BFRs such as decabromodiphenylethane (DBDPE) as an alternative BFR of DBDE and bis tribromophenoxy ethane (BTBPE) are analyzed also.

Analysis: Throughout the extraction, cleanup and analysis procedures, the brominated compounds were protected from degradation by light by using amber glassware or UV cut off light. Approximately 1 g of blubber was Soxhlet-extracted for 12 hours using dichloromethane. The sample clean-up procedure is depicted in Figure 1. Prior to cleanup procedure individual BFR are examined for development of methodology. Recovery of $^{13}C_{12}$-labelled internal standard were more than 80%. For the polar fraction, ethylating was applied for hydroxyl metabolite compound. Following step performed analysis of BFRs. (1) HRGC/LRMS NCI scanning for search of brominated compounds, (2) HRGC/LRMS EI scanning for identification or unknown compounds, (3) HRMS scanning for accurate mass measurement and identification molecular formula, (4) HRGC/HRMS in EI-SIM using all commercially available $^{13}C_{12}$-labelled internal standard for target compound quantification. Detailed analysis information of PBDEs was reported elsewhere[7, 8]. Identification and quantification of BFRs was performed using HP 6890 Series high-resolution gas chromatography interfaced with a Micromass Autospec - Ultima high-resolution mass spectrometer or Thermoelectron/Finnigan MAT 95XL.

Results and Discussion

Figure 2 shows mass chromatogram of m/z=79 for brominated organic compounds in standard solution and Finless Porpoise sample by HRGC/LRMS NCI scan.

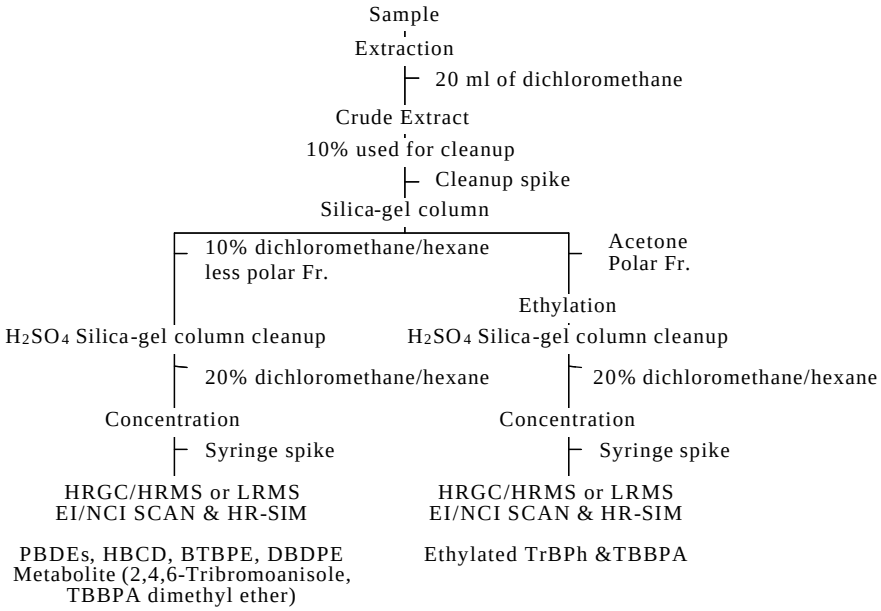

Figure 1. Cleanup procedure for BFR

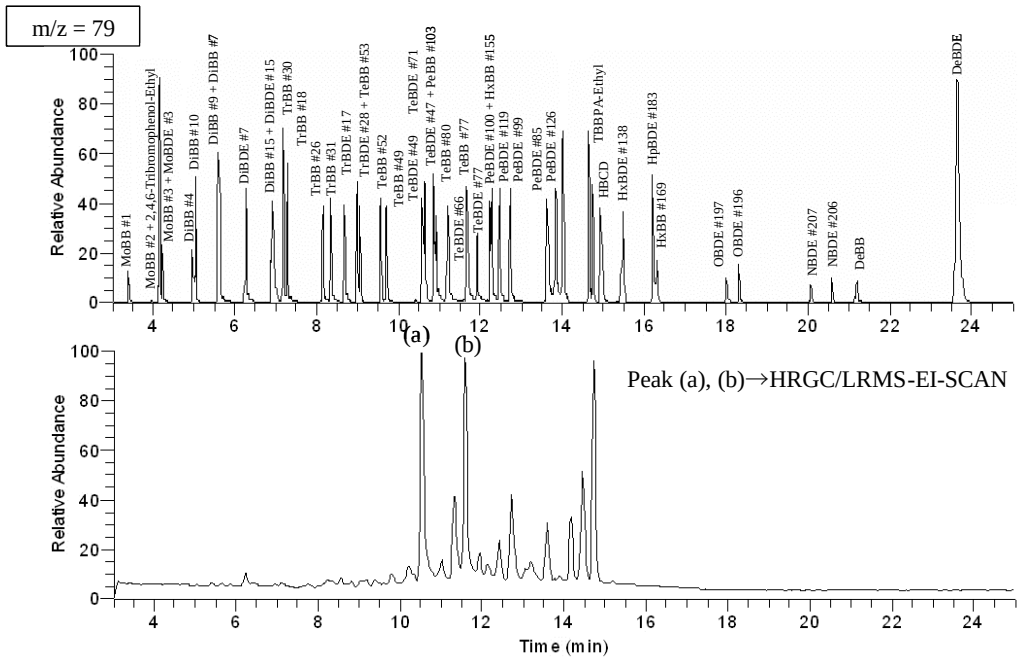

Figure 2. Mass chromatogram of m/z = 79 for brominated organic compounds by by HRGC/LRMS-NCI-scan. standard solution (upper), Finless Porpoise sample (lower)

It ca be detected enough level of brominated compounds in Finless Porpoise sample. Figure 3 shows mass spectrum of peak (a) and (b) in Finless Porpoise sample by LRMS EI scan. Peak (a) is identified tetrabromodipenylether (TeBDE) while peak (b) is unknown mass spectra. From the accurate mass measurement by HRMS scan, peak (b) was probably identified as methoxylated TeBDE (TeBDE-OME) by comparison of theoretical accurate mass spectrum within ±10ppm error (Figure 4). We also detected TeBDE-OME at the same intensity of TeBDE by HRMS mass chromatogram in this sample.

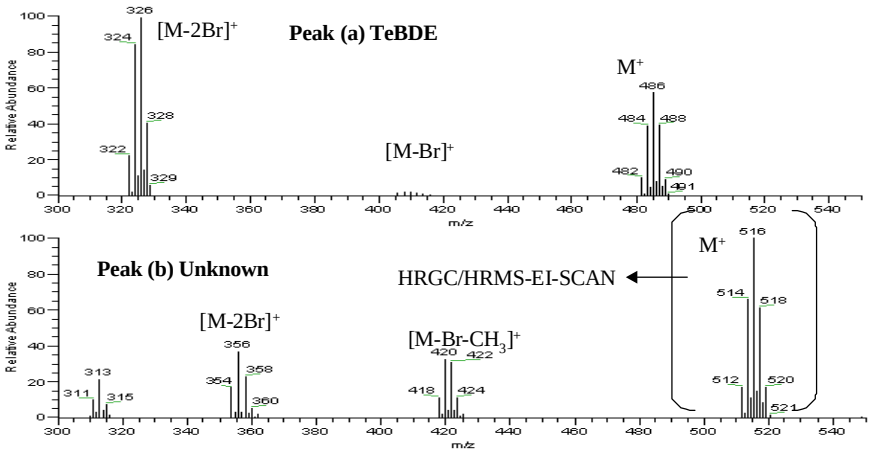

Figure 3. Mass spectrum of peak (a) and (b) in Finless Porpoise sample by HRGC/LRMS-EI-SCAN.

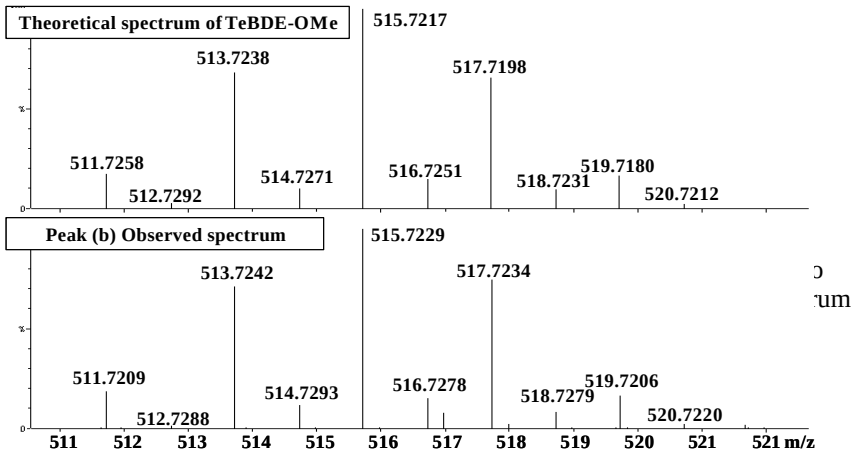

Figure 4. Comparison with accurate mass spectrum of peak (b) and theoretical spectrum by HRGC/HRMS-EI-SCAN

In this sample, BFRs such as PBDEs, HBCD were detected relatively high level, while the concentrations of BDE#47 200 ng/g was the highest among PBDEs detected. BDE209 was also detected although the concentrations were lower than those of other congeners. The concentrations and composition of PBDEs found in the blubber of finless porpoise were similar to those observed in the blubber of coastal cetaceans in Japanese waters[9].

Decabromodiphenylethane (DBDPE) is also detected in the blubber of finless porpoise. To our knowledge, this is a first repot on the detection of DBDPE and the level is higher than DBDE, indicating its increasing use as an alternative BFR of DBDE.

The usage of HBCD, DBDPE and bis tribromophenoxy ethane (BTBPE) are gradually increase since 1990's in Japan. Moreover, TBBPA dimethyl ether and tribromo anisole, which are metabolites of TBBPA and TBP, respectively, are also detected at higher concentrations than their parent compounds.

Consequently, it is necessary to investigate the extent of pollution by these compounds and their accumulation in the ecosystem.

Table 1. Concentration of BFRs in blubber of finless porpoise sample by HRGC/HRMS-SIM

Compound	Concentration (ng/g)
TrBDEs	31
TeBDEs	280
PeBDEs	180
HxBDEs	370
HpBDEs	76
OBDEs	39
NoBDEs	0.22
DeBDE	0.27
TBBPA	0.089
TBBPA-DME [1)]	0.13
TrBPh	0.46
Tribromoanisole	1.1
HBCD	86
BTBPE [2)]	0.10
DBDPE [3)]	7.3

1):TBBPA dimethyl ether
2):Bistribromoohenoxy ethane
3):Decabromodiphenyl ethane

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