

# ANALYSIS OF DECHLORANES AND EMERGING BROMINATED FLAME RETARDANTS WITH A MULTI-COMPOUND MULTI-MATRIX METHOD AND GC-API-MS/MS

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## Introduction

Recently, concerns emerged regarding the potential persistence, accumulation and/or toxicity of halogenated flame retardants (HFRs). Particularly dechlorane plus and other HFRs from the dechlorane group as well as “emerging” (“novel”, “alternative”) brominated flame retardants (eBFRs), are in the focus of interest. In order to assess their background levels in a broad variety of environmental matrices, a comprehensive method was developed using API GC-MS/MS as modern and sensitive instrumental technique. The scope of analysed flame retardants was derived from their actual findings in the arctic environment as a first indicator for their potential ubiquitous distribution<sup>1</sup> and presently enables the determination of 21 HFRs. Additionally, PBDEs as legacy BFRs were also analysed by GC/MS within the developed method. The analytical scheme has been designed to provide a tool for the analysis of a broad range of HFRs in samples from the German Environmental Specimen Bank (ESB), especially biota like plant leaves/needles, marine organisms (bream, mussels and other), birds eggs (herring gull) and riverine suspended particulate matter (RSP).

## Materials and methods

The final method started with a sample preparation consisting of freeze-drying and homogenisation of the samples. The prepared samples were then extracted with Dichloromethane/n-hexane 1:1 v/v using ASE for biota samples and Soxhlet extraction for RSP samples. After extract evaporation and – for RSP samples – treatment with activated copper, a 3-step cleanup was performed by successive column chromatography over silica (Na<sub>2</sub>SO<sub>4</sub>), GPC (Bio-Beads SX-3 with ethyl acetate / cyclohexane 1:1 v/v) and – for biota samples – Florisil fractionation. Instrumental analysis was performed for dechloranes/eBFRs by GC-MS/MS (Waters XEVO-TQS) in API+/dry mode with 1 µL pulsed pressure splitless injection. The GC was equipped with a 15 m DB5-HT, 0.25 mm i.d., 0.1 µm i.d.), pre-column/transfer line and run in CP mode at 1 mL min<sup>-1</sup> followed by a ramped flow segment with flow ramped at 1 ml min<sup>-1</sup>\*min<sup>-1</sup>. For PBDEs, analysis was done by GC/MS (Agilent 6890GC/5973MS) on a 15m RTX1614 column using 3 µL splitless injection in CP mode. Quantification was performed by isotope dilution quantification with 8 mass-labelled internal standards. For a schematic overview see table 1; the detailed method is described elsewhere<sup>2</sup>.

Method development took place using surrogate matrices first hand, being hen’s egg (for birds eggs, e.g. herring gull), fish homogenate/fish oil (for marine organisms) and spruce needles collected from *Picea abies* and *P. pungens* (for plant leaves/needles). The final method was validated in 4 complete method validation cycles on surplus sample materials from supplies of the German Environmental Specimen Bank: spruce needles, bream fillet, riverine suspended particulate matter, herring gull eggs. For validation, the materials were fortified with native analytes at standard addition levels of 100 (DBDPE: 1000) pg per sample for dechloranes/eBFRs and 1200 (Hx-OcBDE: 2400; No-DcBDE 6000) pg per sample for PBDEs. As results, among others, intra-day precisions, intermediate precisions and an estimation of measurement uncertainties were generated.

## Results and discussion

The method development included the examination of the suitability for different cleanup- and analytical techniques and resulted in a GC-MS/MS-method which enabled the detection of compounds with high (e.g. DBDPE) and low (e.g. TBA) boiling points and different polarities. Starting point of the method development was the selection of possibly suitable MS detectors. In a comparison, a API-GC-MS/MS system (XEVO-TQS, Waters) was preferred over a GC-HRMS system (Autospec Ultima, Waters) which was similarly sensitive and a GC-MS/MS (7000C, Agilent). Also, API-GC-MS/MS was already used for HFRs<sup>3</sup>. The GC-MS/MS method had very good performance; linearity was excellent, mainly in the range of 0.01 to 40 pg µL<sup>-1</sup> (table 1). Using isotope dilution quantification/isotope labelled standards, the working range was nevertheless restricted to a

narrower range because of RRF stability. The basic detection capability of the XEVO-TQS API-GC-MS/MS was for several compounds often lower (down to 0.002 pg  $\mu\text{L}^{-1}$ ), but performance stability (e.g. ion ratios, peak performance) in the low fg range was critical. Also, brominated FRs tended to easily adsorb or degrade within the GC system (viz. injector, pre-column/column, transfer line) whereas chlorinated compounds such as the dechloranes gave excellent signals (figure 2)

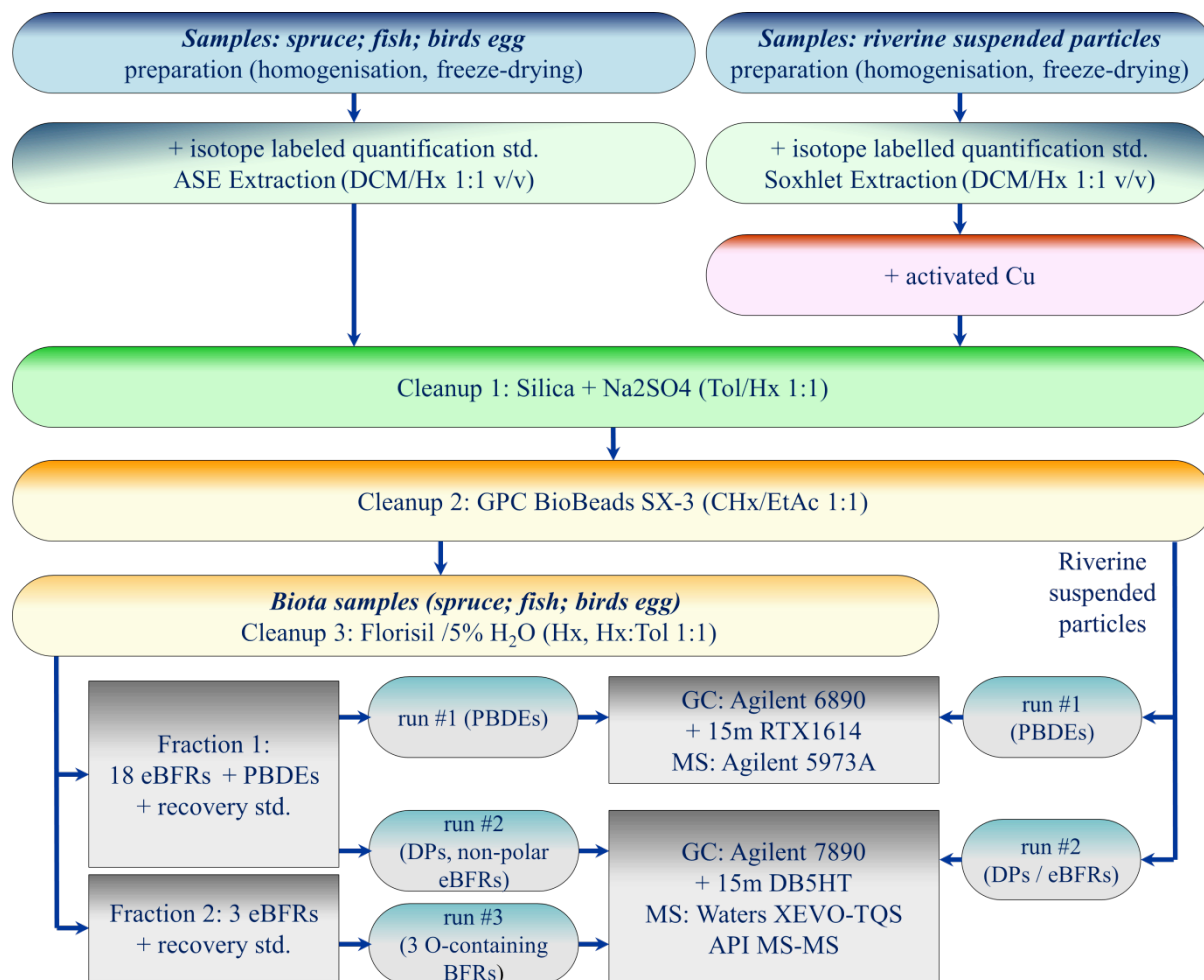


Figure 1: schematic method overview (Hx = n-hexane, Tol = toluene, EtAc = ethyl acetate, DCM = dichloromethane)

The method cleanup was designed to include the possibility to analyse DPMA, ATE and other substances which proved to be acid-labile<sup>4</sup>. The whole procedure resulted in an overall performance which is satisfactory for a multi-compound multi-matrix method given the completely different behaviours of the single matrices. The overall method quality is emphasised by good recovery rates for the used isotope-labelled quantification standards (figure 3) which are within the acceptable range of 50% to 130% with only few exceptions which might be due to matrix effects.

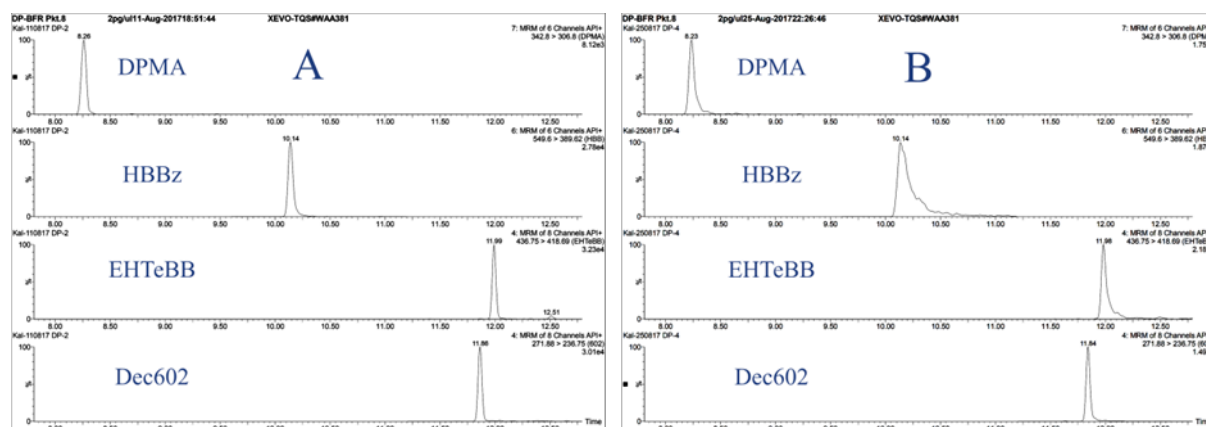


Figure 2: gaschromatographic behaviour of brominated and chlorinated HFRs. A = freshly installed GC column, B = GC column after 40 sample injections

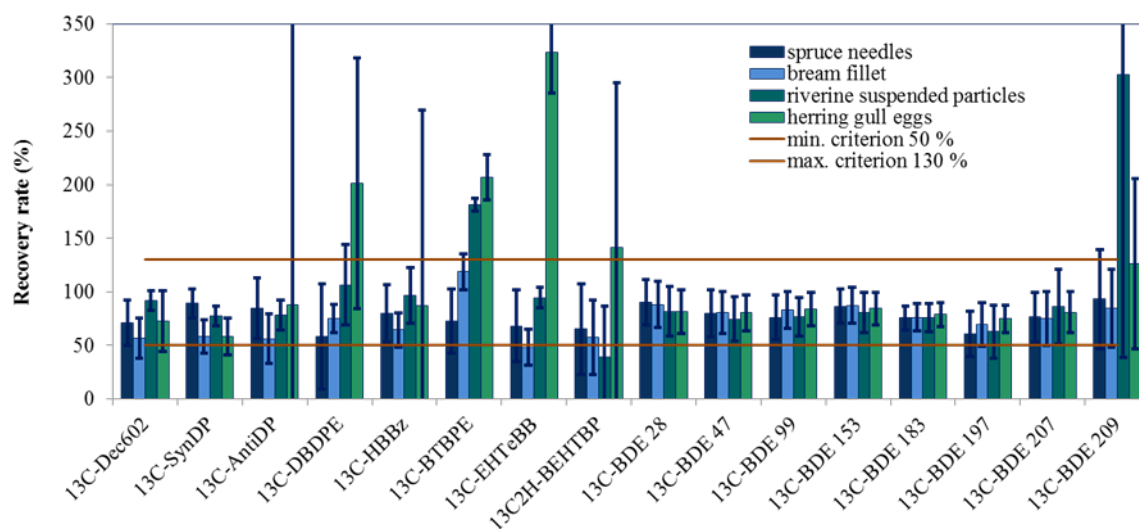


Figure 3: recoveries of  $^{13}\text{C}$ -labelled internal standards

Validation results were generally good seeing the fact that 4 different real sample materials have been used. These were analysed beforehand, resulting in patterns of background findings which led to an additional term in the result calculations for measurement uncertainty. The native standard addition levels of the DPs and eBFRs were designed to compromise for analyte LOQs and sensitivity on one hand (table 1) and for levels derived from the expected order of magnitude for possible findings on the other hand. The method for PBDEs was adapted from available routine methods, integrating them into sample preparation and cleanup of the presented method. The method carries the capability to be extended to the analysis of many other flame retardants, provided their volatilities fall within the already examined range (e.g. TBA as early eluter on a 15m-GC column vs. DBDPE or PBDE #209 as very high boiling, highly brominated and thermally labile compounds). Other compounds, e.g. the more polar phenolic compounds, might require additional developmental work, because the present method version has limitations there. Further experiences during method development showed the presence of remaining matrix interferences even after a three-step cleanup. This, together with their unfavorable mass fragmentation (only ions of relatively low mass formed) led to the exclusion of  $\beta$ - and  $\gamma$ -TBECH from the method's scope during validation.

First results from the application of the method to samples from the German ESB are already being published.

Analyte	IDL			working range		CC	MQL	Labelled std.			relative sensitivity
	min	min	max	r <sup>2</sup>	pg per sample			reference	RRF avg.	RRF SD	
	pg*μL <sup>-1</sup>	pg*μL <sup>-1</sup>	pg*μL <sup>-1</sup>			%					
Syn-DP	0,01	0,02	40	0,9999	24	<sup>13</sup> C-Syn-DP	9,979	0,789	8%		0,4
Anti-DP	0,01	0,02	40	0,9999	27	<sup>13</sup> C-Anti-DP	2,030	0,260	13%		0,4
Dec602	0,01	0,05	40	0,9997	7	<sup>13</sup> C-Dec602	3,481	0,422	12%		1
Dec603	0,01	0,05	100	0,9998	3	<sup>13</sup> C-Dec602	2,045	0,248	12%		1
Dec604	0,02	0,05	100	0,9999	5	<sup>13</sup> C-Dec602	1,136	0,183	16%		0,5
Cl <sub>10</sub> -AntiDP	0,01	0,02	40	0,9997	2	<sup>13</sup> C-Syn-DP	18,920	2,593	14%		1
Cl <sub>11</sub> -AntiDP	0,01	0,02	40	0,9995	1	<sup>13</sup> C-Anti-DP	4,137	0,322	8%		1
DPMA	0,02	0,02	40	0,9997	1	<sup>13</sup> C-HBBz	0,640	0,104	16%		0,2
DBDPE	0,5	10	1100	0,9953	900	<sup>13</sup> C-DBDPE	0,934	0,128	14%		0,005
HBBz	0,01	0,05	40	0,9997	10	<sup>13</sup> C-HBBz	1,401	0,166	12%		0,5
PBT	0,01	0,05	40	0,9999	43	<sup>13</sup> C-HBBz	1,983	0,300	15%		0,2
PBEB	0,01	0,05	40	0,9999	3	<sup>13</sup> C-HBBz	3,158	0,500	16%		1
ATE	0,02	0,05	40	0,9998	52	<sup>13</sup> C-HBBz	0,653	0,106	16%		0,1
BATE	0,1	0,1	40	0,9997	17	<sup>13</sup> C-HBBz	1,110	0,165	15%		0,1
DPTE	0,05	0,5	40	0,9996	322	<sup>13</sup> C-HBBz	0,561	0,077	14%		0,5
TBA	0,01	0,02	20	0,9998	170	<sup>13</sup> C-HBBz	13,883	2,590	19%		1
β-TBECH	0,01	0,05	20	0,9988	11	<sup>13</sup> C-HBBz	2,670	0,284	11%		0,1
γ-TBECH	0,02	0,02	20	0,9966	14	<sup>13</sup> C-HBBz	1,170	0,121	10%		0,2
BTBPE	0,2	0,2	200	0,9965	99	<sup>13</sup> C-BTBPE	0,752	0,066	9%		0,2
EHTeBB	0,05	0,2	200	0,9996	133	<sup>13</sup> C <sup>2</sup> H-EHTeBB	0,808	0,155	19%		0,2
BEHTBP	0,05	0,2	200	0,9995	460	<sup>13</sup> C <sup>2</sup> H-BEHTBP	0,234	0,038	16%		0,1

Table 1: working range, instrument detection limit (IDL), method quantification limit (MQL), calibration and sensitivity data. RRF = relative response factor, CC = correlation coefficient

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