

Instrumental analysis of brominated POPs

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Today's Presentation

1. *Introduction*
2. *A simplified GC method to analyze POP-BFRs in plastics*
3. *Inter-lab Study on POP-BFRs in plastics*

Brominated POPs Used as Plastic Additives

	Main use	Contents added to products	EU RoHS directive maximum concentration	Low POP content for waste under the Basel Convention
PentaBDE	Polyurethane foam, printed circuit board	Up to 40% by weight (1% = 10,000 mg/kg)	1,000 mg/kg as a sum (mono- to decaBDE)	[50 mg/kg] or [500 mg/kg] or [1,000 mg/kg] as a sum of POP-BDEs
OctaBDE	Electronic casing			
DecaBDE	Electronic casing, textile coating, building insulation			
HBCD	Textile, building insulation	Up to 5% by weight in textile, ~0.5% in EPS, ~5% in XPS	<i>Not applicable</i>	100 mg/kg [or 500 mg/kg] or 1,000 mg/kg

➔ Chemical analysis is essential to identify products and wastes containing POPs.

➔ POP contents in product and wastes >>> atmosphere, breast milk

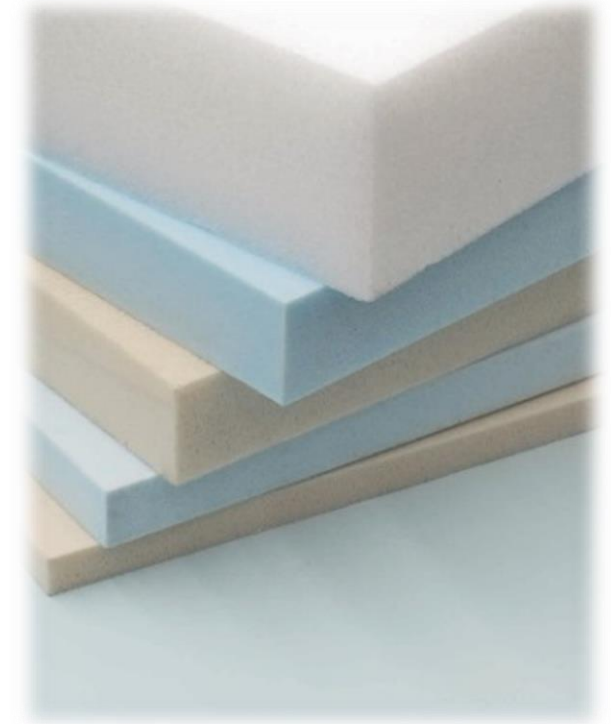
PBDE and HBCD in Plastic Products and Wastes



CRT TV casing:
~ 120,000 mg/kg of PBDE

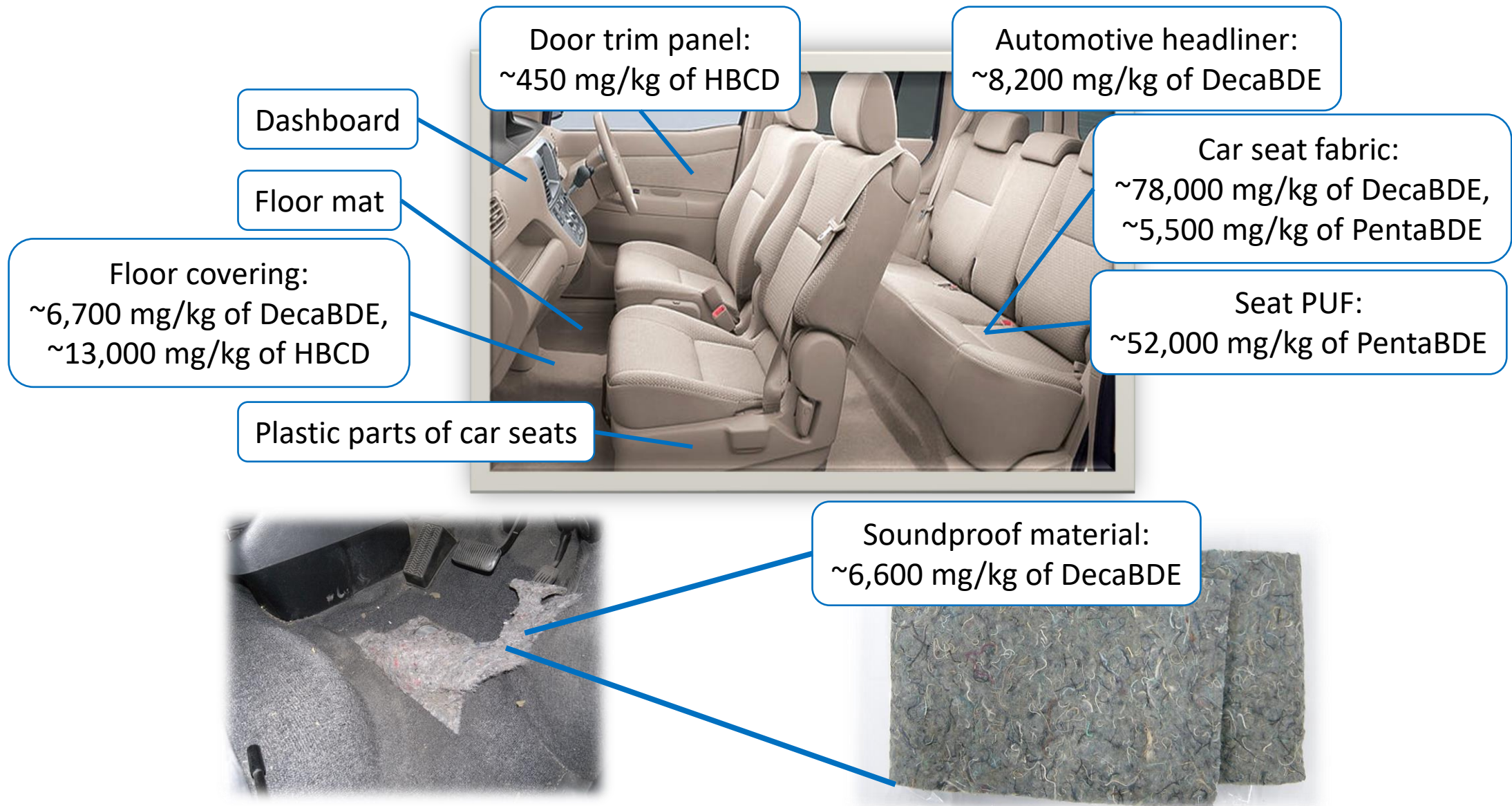


Flame-retarded curtains:
• 22,000–43,000 mg/kg of HBCD
• 120,000 mg/kg of PBDEs

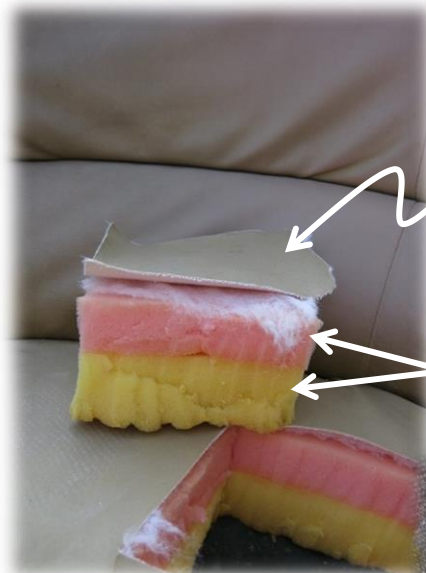


Building insulation foam:
• Expanded polystyrene (EPS): ~5,500 mg/kg of HBCD
• Extruded polystyrene (XPS): ~44,000 mg/kg of HBCD

PBDE and HBCD Found in End-of Life Vehicles



Sofas and Couches



Seat fabric

Polyurethane foam (PUF):
1,800 mg/kg of PBDEs



PUF chips

Infant and Child Car Seats



Seat fabric:
~920 mg/kg of PBDE

Polyurethane foam:
~23,000 mg/kg of PentaBDE,
~43,000 mg/kg of DecaBDE



EPS:
3,800–10,000 mg/kg of HBCD



A simplified method to analyze POP-BFRs in Plastic

Eguchi A., Matsukami H., Takahashi A., Kajiwara N. (2021) Simultaneous determination of polybrominated diphenyl ethers and hexabromocyclododecane in plastic waste by short-column gas-chromatography-quadrupole mass spectrometry and electron capture detector. *Chemosphere* 277, 130301.

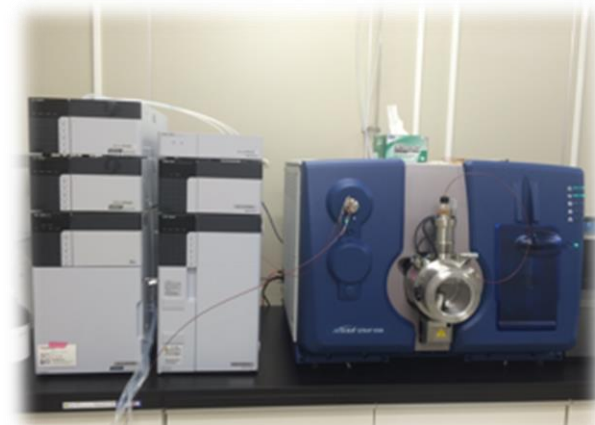
Instruments Used for PBDE and HBCD Analysis

	Tentative Baseline LPC (mg/kg)	Conventional precise method	Proposed simplified method
PBDE	[50 or 500 or 1,000 as a sum]	GC-HRMS, GC-MS/MS etc.	Simultaneous determination by GC-qMS and GC-ECD
HBCD	100 or 1,000	LC-MS/MS (isomer specific analysis)	

General-purpose equipment, not state-of-the-art



GC-high resolution mass spectrometry



Liquid chromatography-tandem mass spectrometry (LC-MS/MS)

A Rapid Simplified Method for POP-BFRs in Plastic Waste

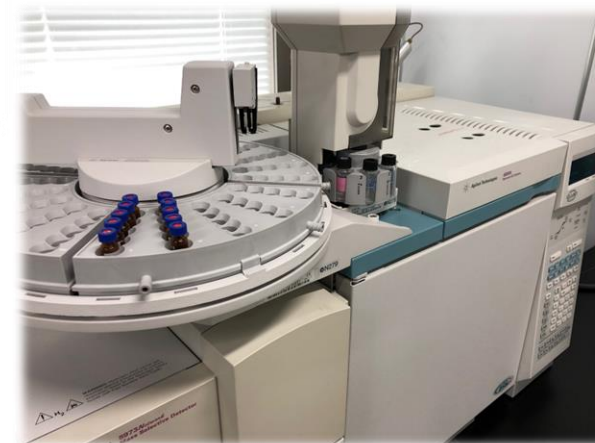
	Tentative Basel LPC (mg/kg)	Conventional precise method	Proposed simplified method
PBDE	[50 or 500 or 1,000 as a sum]	GC-HRMS, GC-MS/MS etc.	Simultaneous determination by GC-qMS and GC-ECD
HBCD	100 or 1,000	LC-MS/MS (isomer specific analysis)	

General-purpose equipment, not state-of-the-art

- A custom shortened DB-5HT GC column (5 m x 0.25 mm i.d., 0.10 μm , cut from a 15-m column)

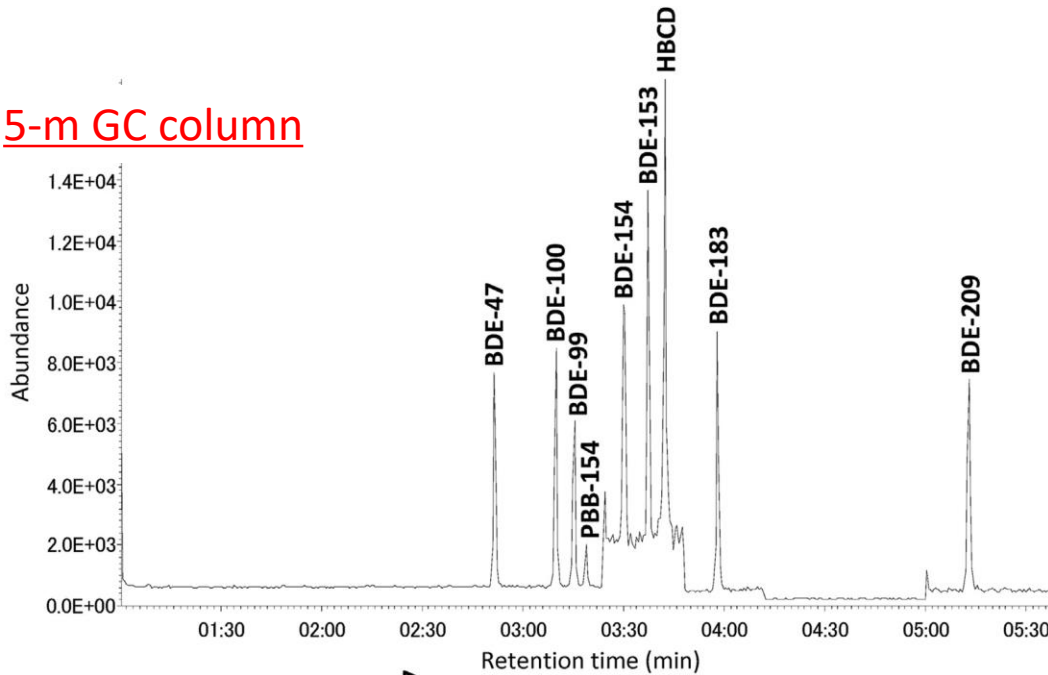


- ✓ Cost reduction
- ✓ Reduction of GC analysis time
- ✓ Reduced impact of pyrolysis

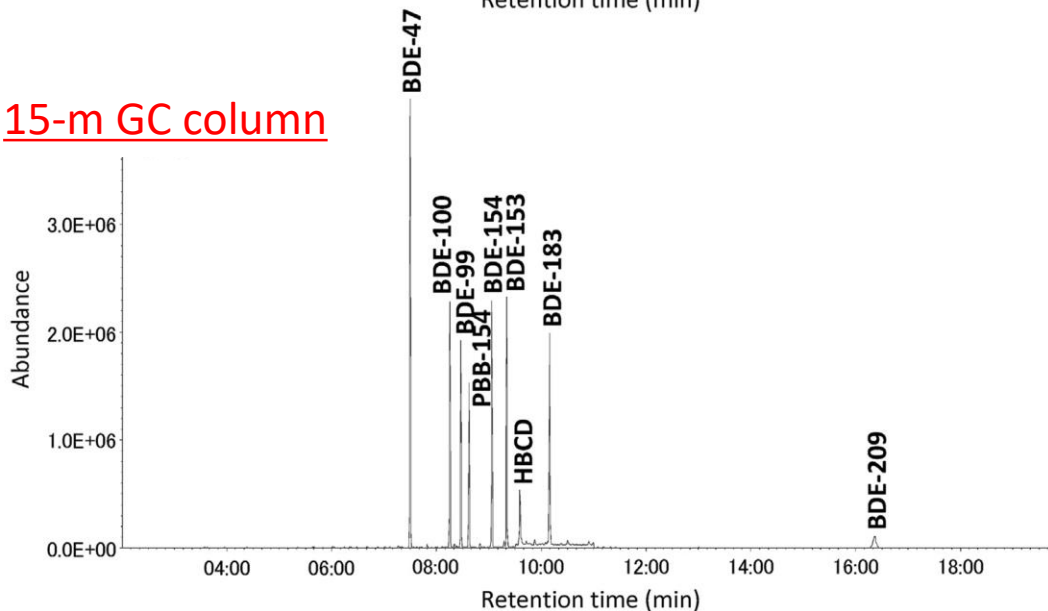


Comparison of GC Chromatograms of POP-BFR Standard Mix.

5-m GC column

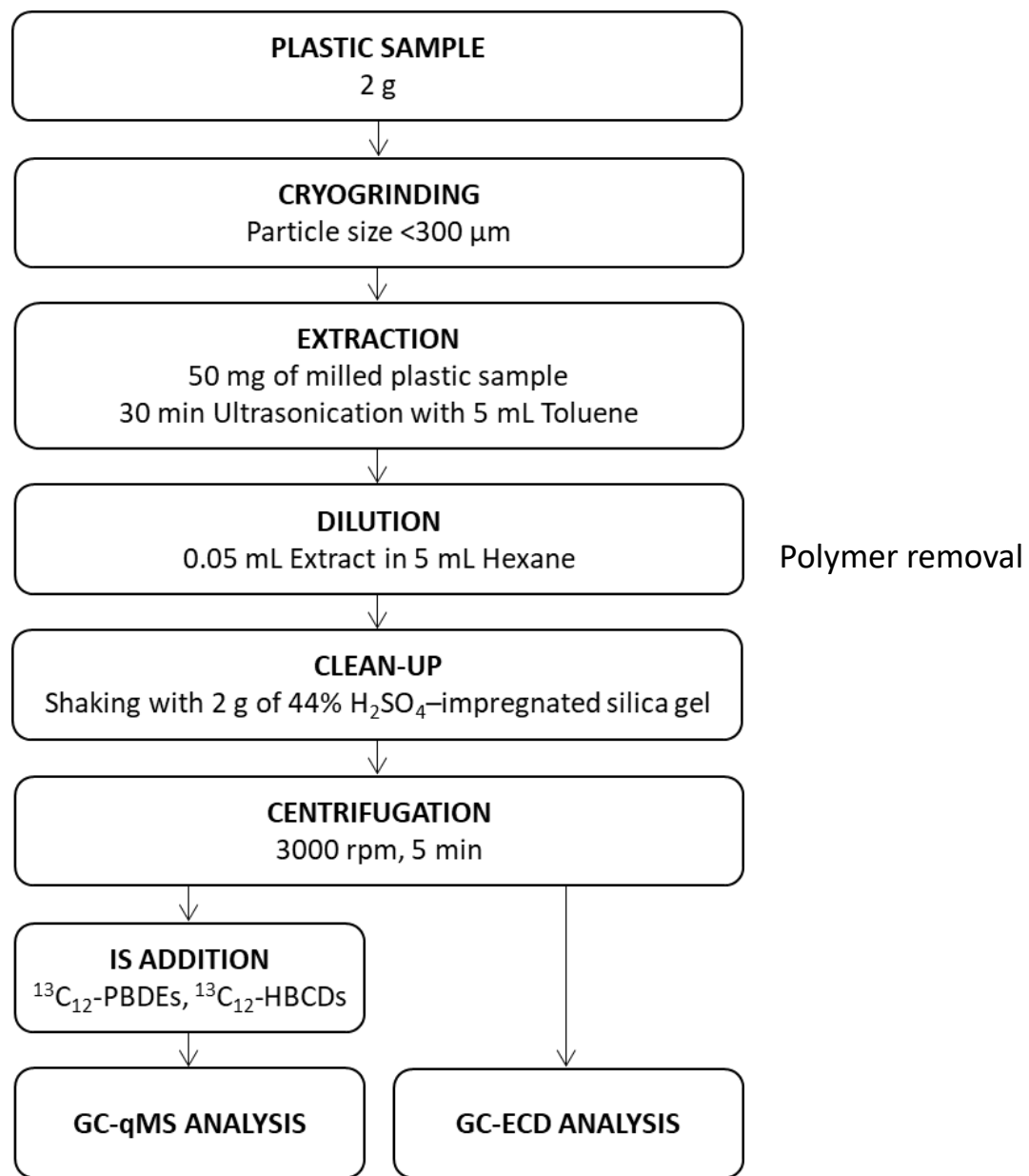


15-m GC column



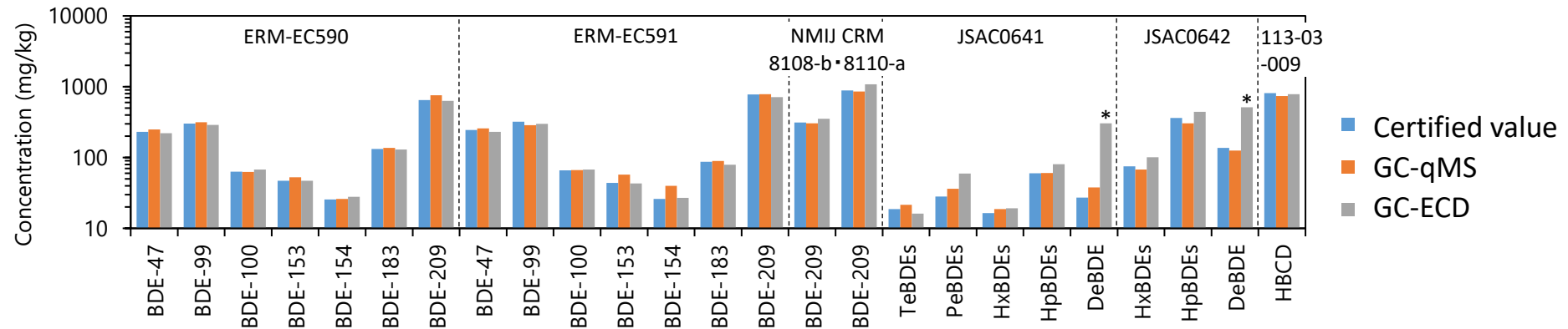
- Major isomers well separated
 - 10 min faster retention time of BDE 209
 - Increased sensitivity of BDE 209
- ➔ 5-m GC column method can be used for POP-BFR screening

Analytical Procedure for POP-BFR Analysis in Plastics

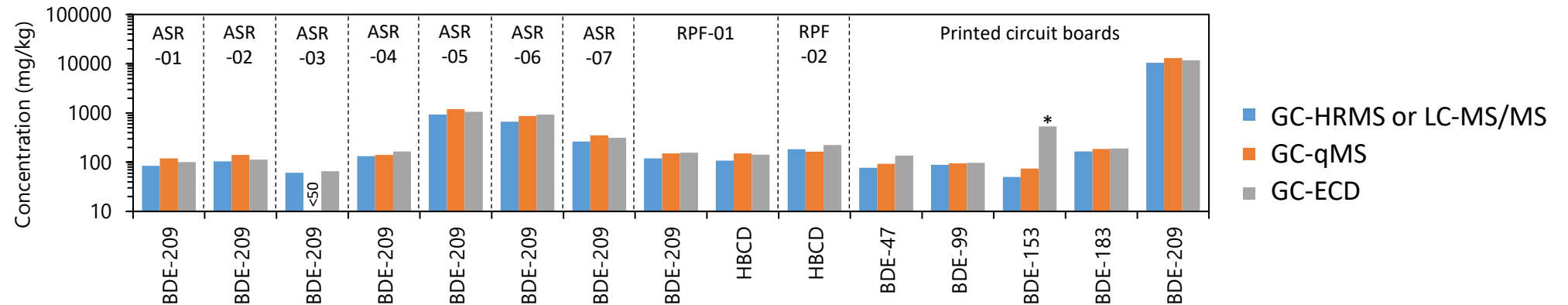


Validation of the Simplified Method

Certified reference materials



Mixed plastic waste samples



- ➔ Within the 30% error ranges of the certified values
- ➔ Can be used as a simplified method specifically for plastics

*interferes could be removed by silica gel

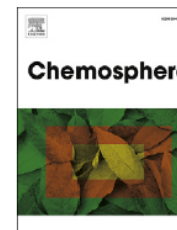


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Simultaneous determination of polybrominated diphenyl ethers and hexabromocyclododecane in plastic waste by short-column gas-chromatography-quadrupole mass spectrometry and electron capture detector



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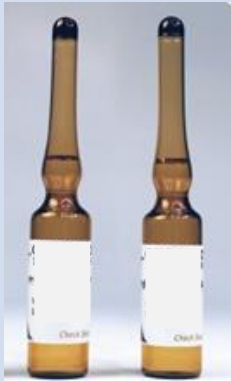




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Inter-lab Study for POP-BFRs in Plastic Waste

Inter-lab Study for POP-BFRs in Plastic Waste

	1 st Round in 2019	2 nd Round in 2020			
Test samples	Standard solutions and plastic extracts 	CRT TV casing 	Car fabric 	Insulation boards (EPS and XPS) 	Extracts of automobile shredder residue (ASR) 
Target compounds	PBDE and HBCD	PBDE		HBCD	PBDE and HBCD
Participants	35 laboratories at universities, research institutes and private companies in Belgium, China, Germany, India, The Netherlands, UK, US, Kuwait and Japan	26 laboratories at universities, research institutes and private companies in Belgium, China, Germany, India, South Korea, the Netherlands, USA and Japan			

The following two methods were used:

- (1) The usual [in-house methods](#) used by each laboratory
- (2) [A simplified GC-qMS or GC-ECD method](#) we propose (Eguchi *et al.*, 2021)