INFLAME

130 years VU UNIVERSITY AMSTERDAM

GC-MS and LC-MS methods for Flame Retardant (FR) analysis

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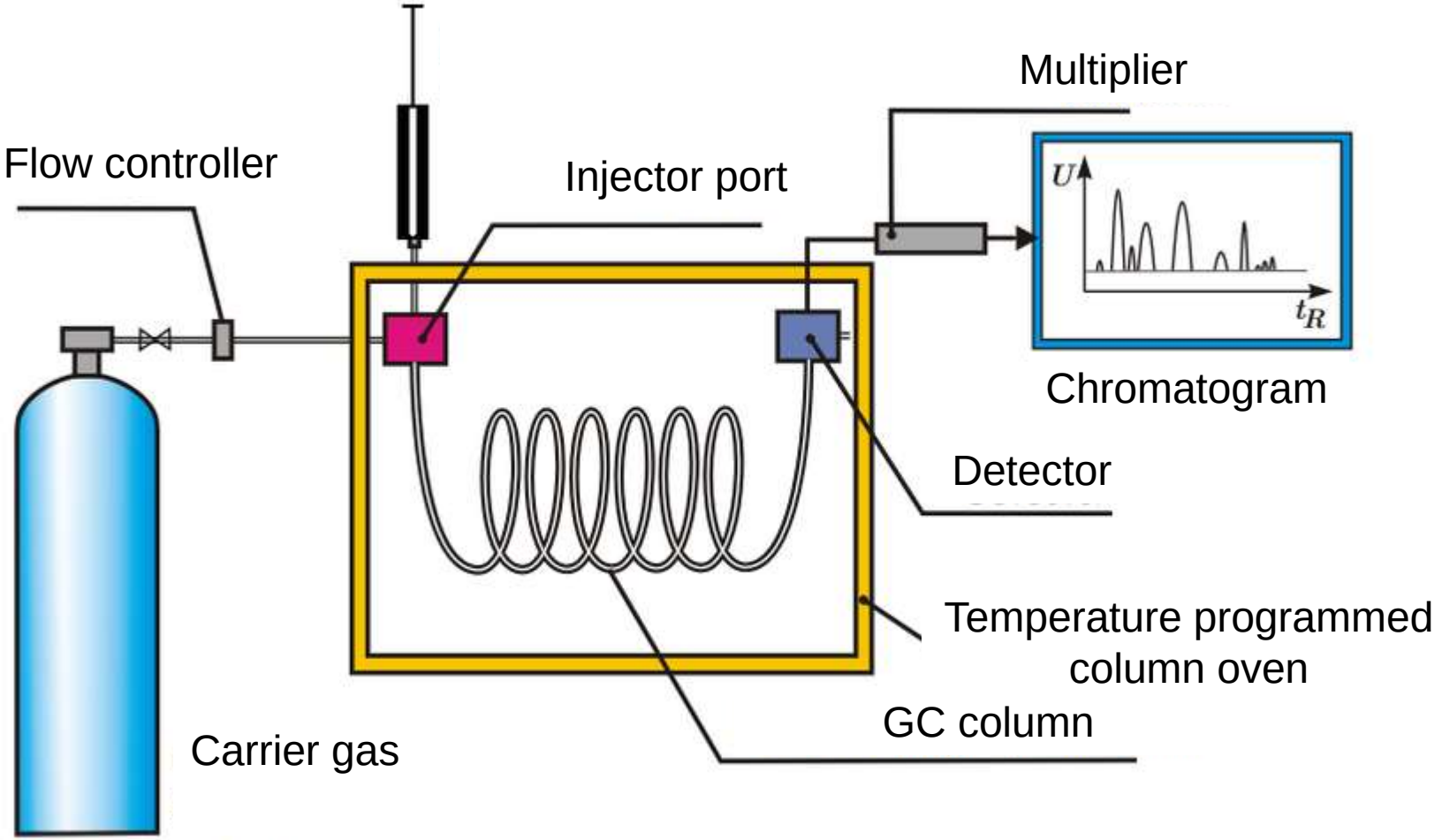
IVM Institute for Environmental Studies

Outlines

- Gas Chromatograph
- Different detectors ECD FID NPD and MS
- Focus on Mass spectrometry
- Different GC parameters
- BFRs PBDEs, BDE209, TBBP-A and HBCD
- “New” compounds PFRs, DBDPE, BTBPE, TBPH, TBB and, PBT

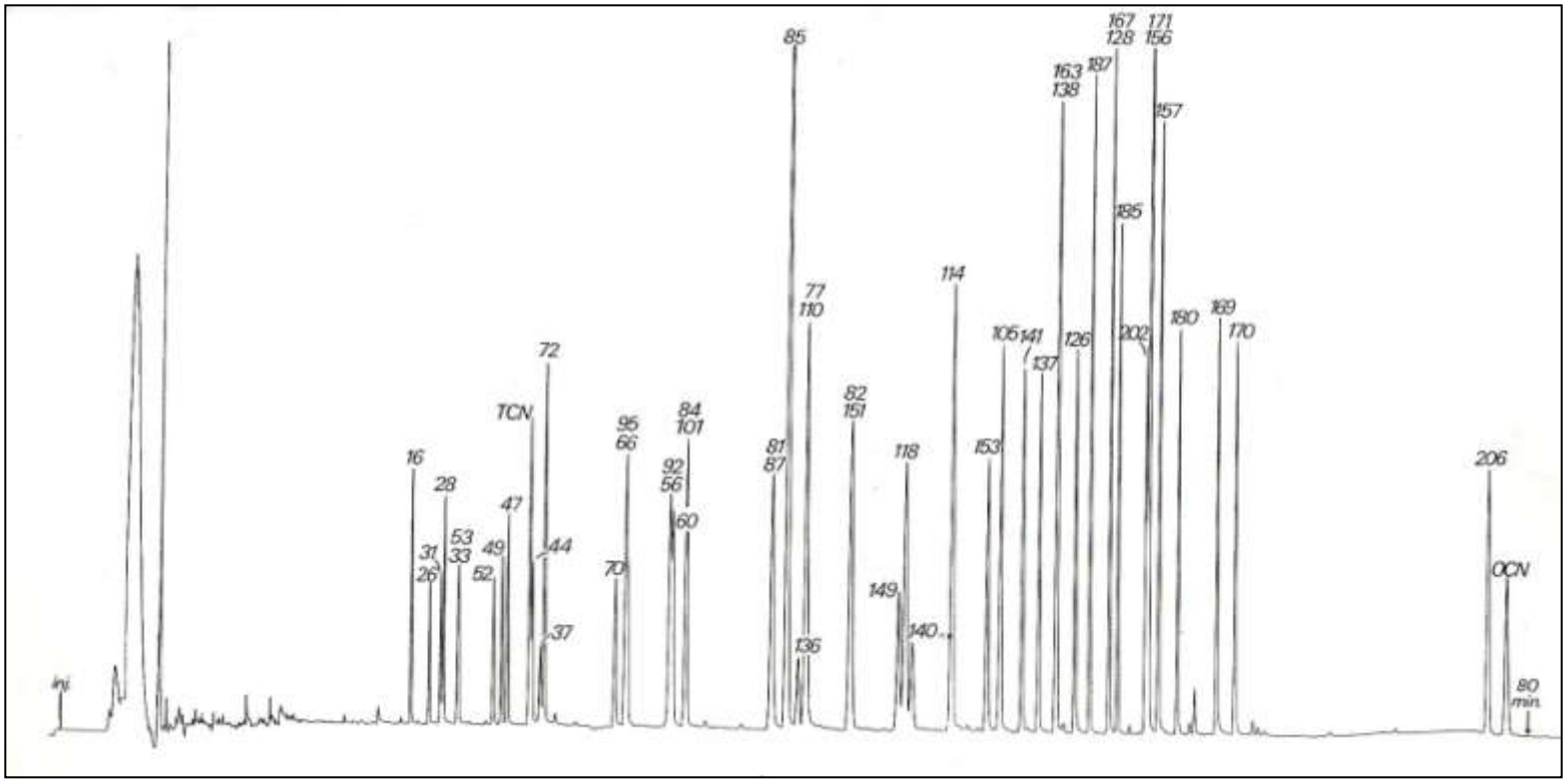
Gas chromatograph



GC-Detectors

- Flame Ionisation detector (FID)
  - Sensitive for detecting hydrocarbons
  - Not really selective measures all flammable compounds
- Electron Capture Detector (ECD)
  - Sensitive to halogens and nitro compounds
  - Low linear range compared to FID
- Nitrogen Phosphorous Detector (NPD)
- Very sensitive but selective detector that responds almost exclusively to nitrogen and phosphorous compounds

ECD chromatogram



- Low selectivity: coeluting compounds can not be separated

Mass Spectrometry (1)

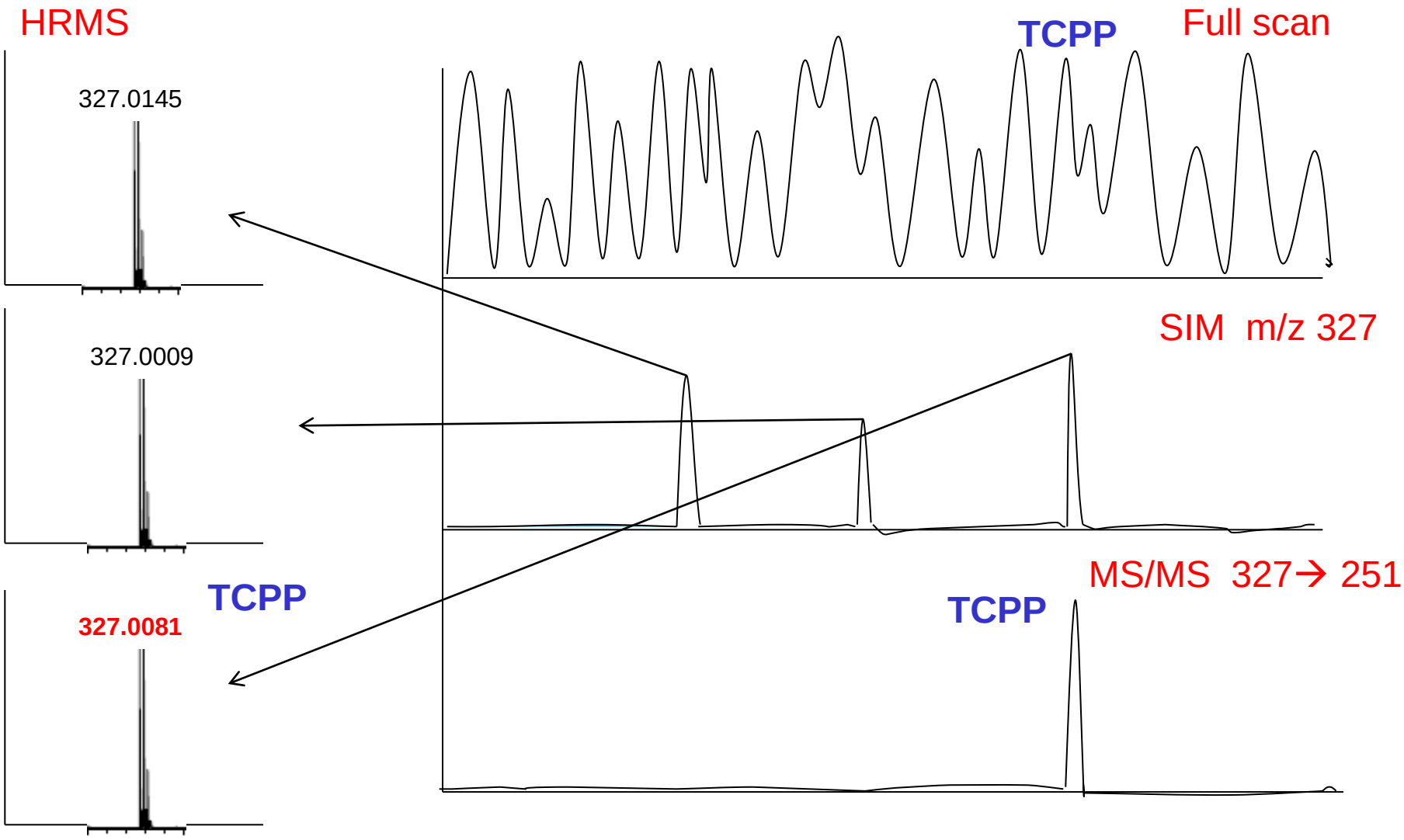
- Electron Impact (EI)
  - Hard ionisation fragmentation of the molecular ion
  - Library search for EI spectra

- Chemical ionisation (CI)
  - Soft ionisation clear spectrum of the Molecular ion
  - Use of reagent gas (Methane)
  - Positive PCI or negative ECNI mode
  - ECNI very sensitive for PBDEs

Mass Spectrometry (2)

- MS
  - Quadrupole (SIM or SCAN)
  - Ion trap
  - Time Of Flight (TOF)
  - Sector instruments (magnet)
- Tandem Mass spectrometry (MS/MS)
  - Two analysers coupled by an collision cell

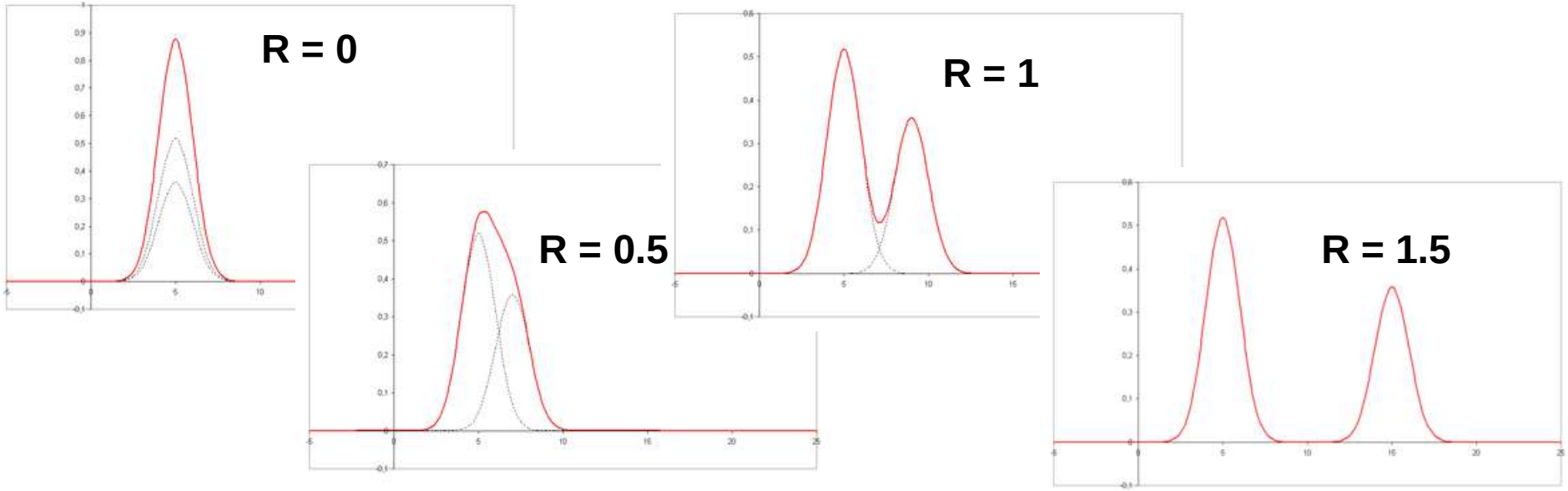
Mass Spectrometry (3)



GC parameters

- Selection of the Stationary Phase
- Column Dimension
- Temperature Program
- Linear Gas Velocity
- Type of Carrier Gas

Resolution



$R = \Delta t_R \times 2 / (W_1 + W_2)$ or $R = \sqrt{N} / 4$

- Improving the resolution:

  Changing mobile phase composition
  Changing column temperature
  Changing composition of stationary phase
  Changing the column length

Selection stationary phase

polarity scale	Stationary phase	brand and type names
5	100% Dimethyl polysiloxane	ZB-1 MS, CP-Sil 5 CB, DB-1, HP-1 MS, RTX-1
8	5% Phenyl-(arylene)- 95% methyl polysiloxane	ZB-5 MS, CP-Sil 8 CB, DB-5 MS, HP-5 MS, RTX-5 MS
17	50% Phenyl-50% methyl polysiloxane	ZB-50, DB-17 MS, HP-17, RTX-50
19	14% cyanopropyl-phenyl/86% dimethylpolysiloxane	CP-Sil 19 CB
24	75% Phenyl-25% methyl polysiloxane	ZB-50, CP-Sil 24 CB
52	polyethylene glycol	ZB-WAX, DB-WAX, CP-WAX 52 CB
88	100% 3-cyanopropylpolysiloxane	BPX70, CP-Sil 88 CB, RTX-2330

- The most widely used stationary phases for halogenated pollutants are: DB-1, DB-5, BPX-5, HT-8, CP-Sil8 CB or CP-Sil 19 CB

Column Dimensions

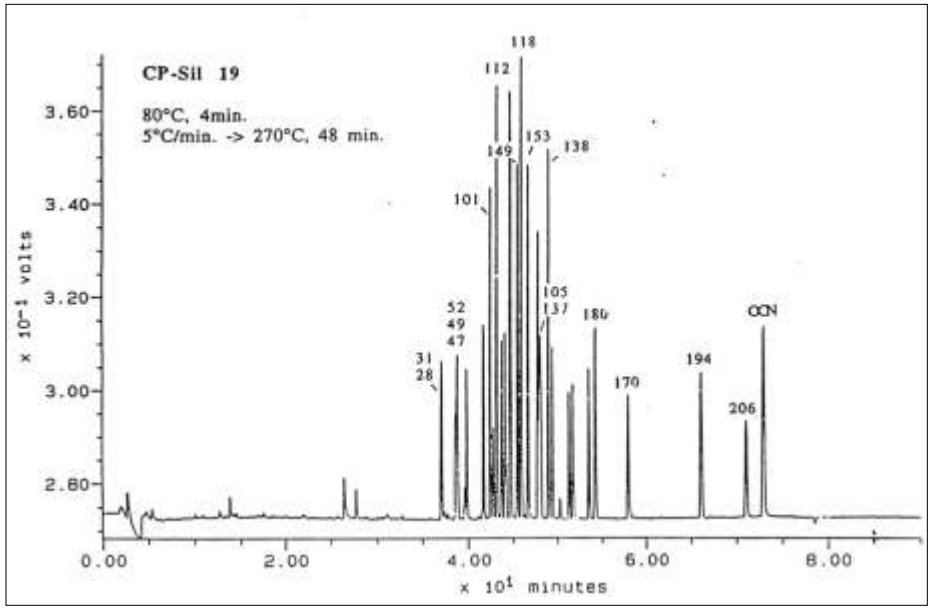
- Effect of Diameter (ID): Stronger than that of Length

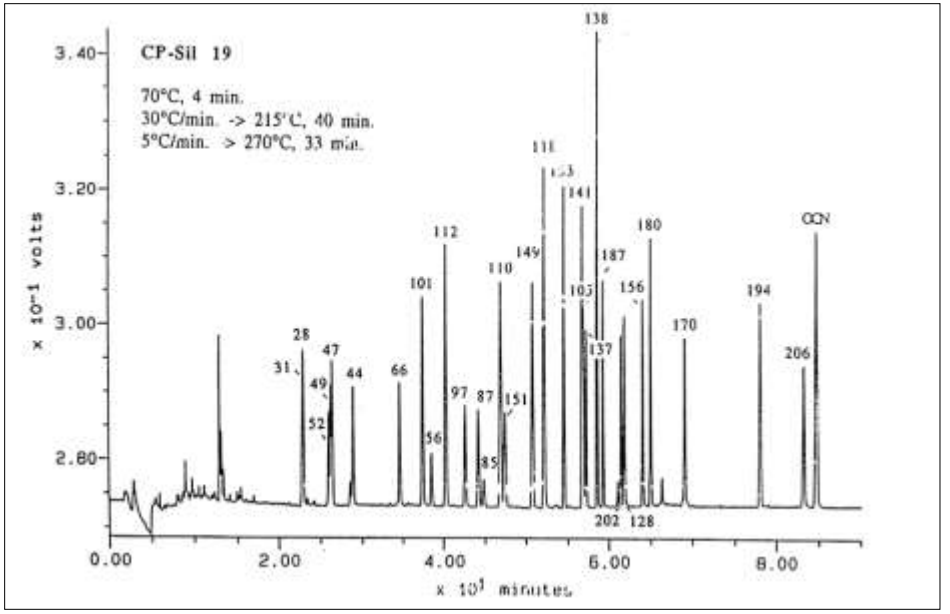
  - **Length**:
    > 100m: to much pressure required, too long retention times,
    < 25: serious loss of separation

  - **ID**:
    <0.10 mm: hardly possible (columns >20m)
    >0.25 mm: serious loss of separation

  - **Film Thickness**:
    < 0.1 μm: risk for degradation due to poor coating
    > 0.3 μm: long retention times, risk for tailing peaks

Temperature Program





Temperature program: 4 min, 80°C; 5°C/min to 270; 48 min 270°C.

Temperature program: 4 min, 70°C; 30°C/min to 215°C; 40 min 215°C; 5°C /min to 270°C; 33 min 270°C

The Optimum mobile phase velocity

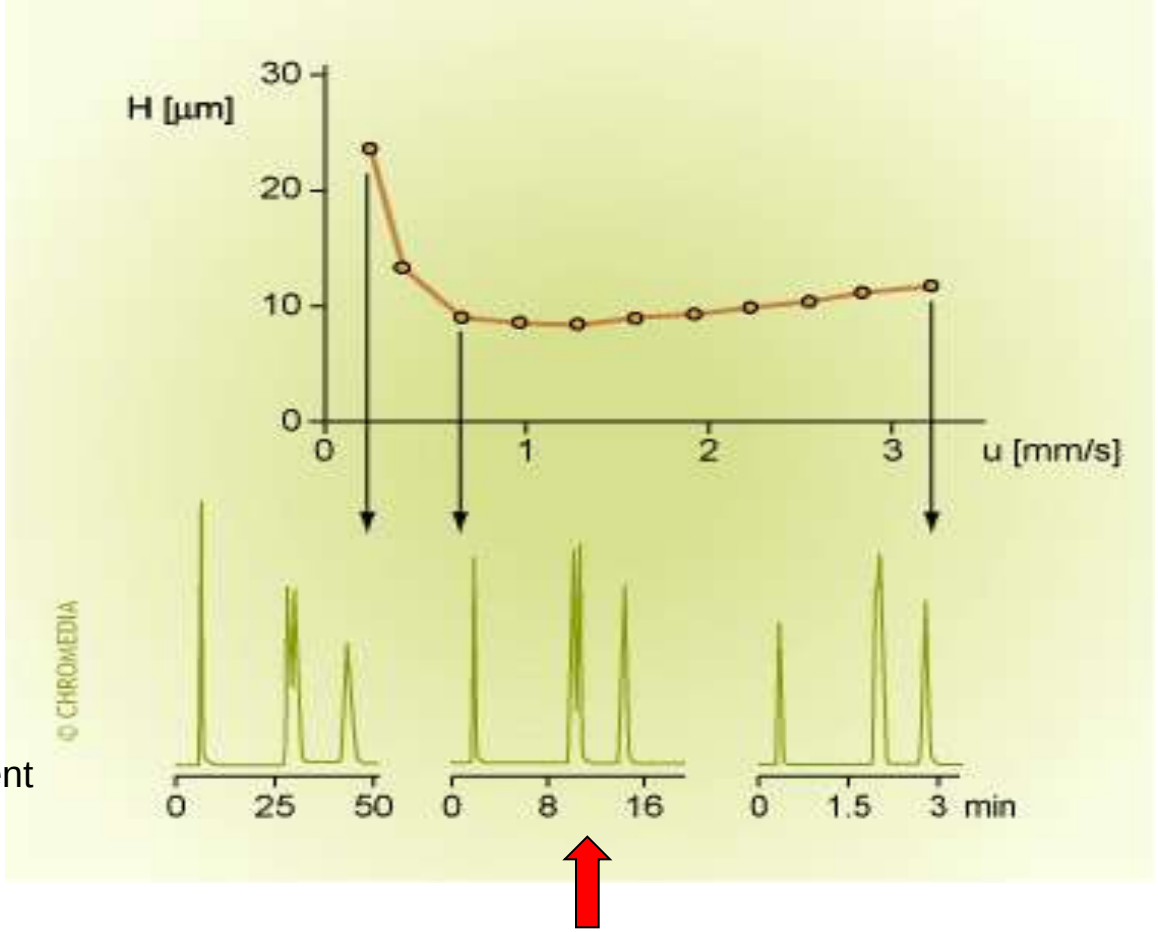
The H-u curve is very useful to determine the **optimum mobile phase velocity** $\mathbf{u_{opt}}$ at which the highest column efficiency will be attained

$$H = \frac{L}{N}$$

Van deemster equation

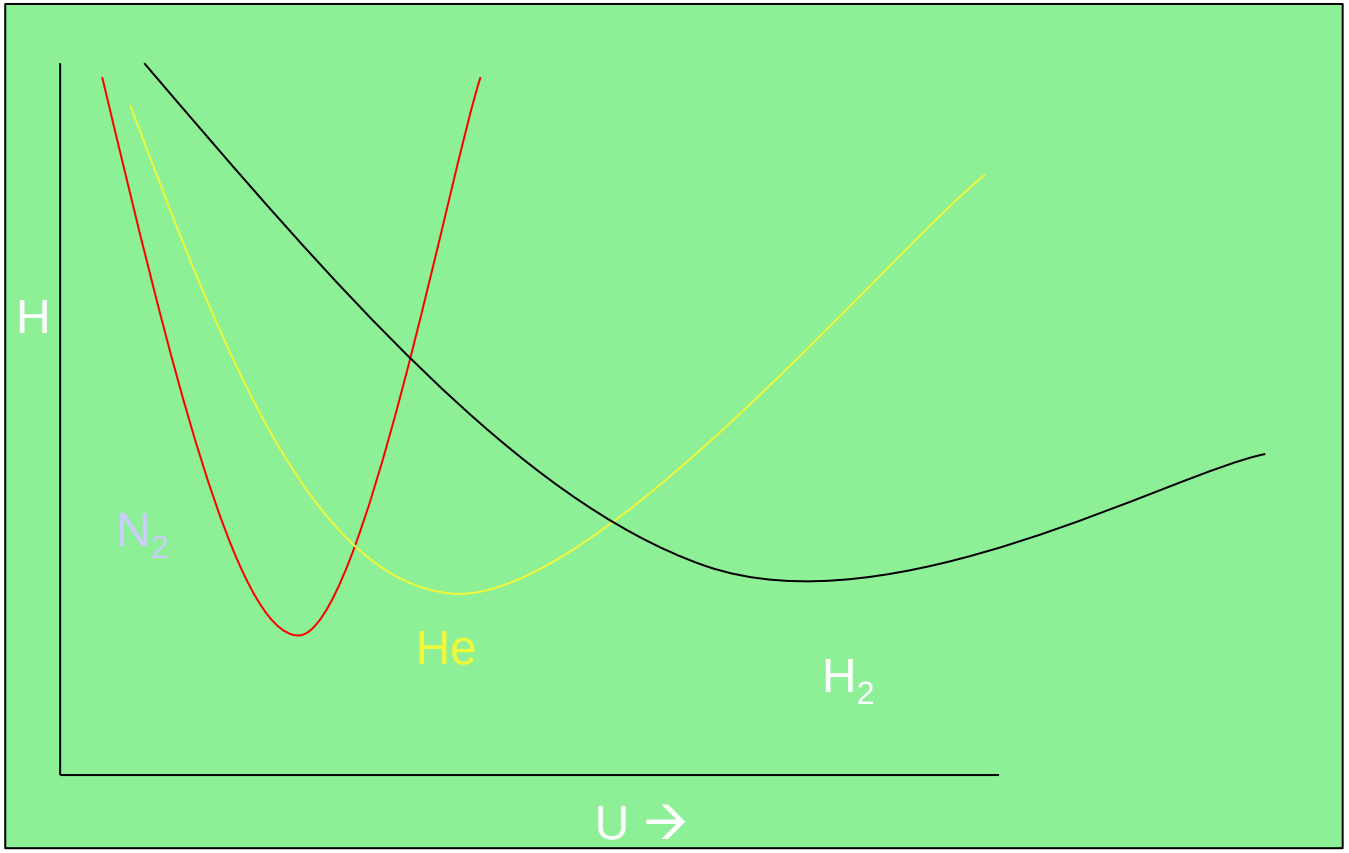
$$H = A + \frac{B}{u} + C \cdot u$$

H = HETP (plate height)
A = Eddy diffusion term
B = Longitudinal diffusion term
u = Linear velocity
C = Resistance to mass transfer coefficient
N = Plate number
L = Column length



Optimum resolution

Selection of carrier gas



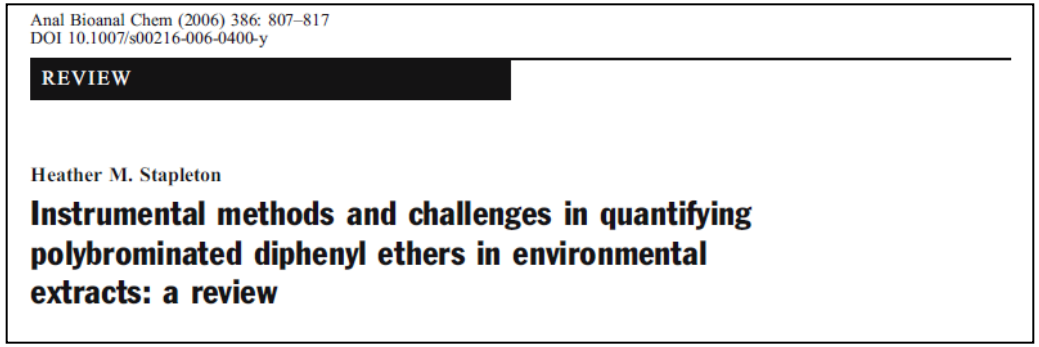
•Hydrogen provide optimum resolution at the highest carrier gas velocity**; optimum separation within an the sorter time**

PBDEs

- PBDEs
  - GC-EI-MS, GC-ECNI-MS, GC/HRMS or LC-MS/MS
    - Advantage and Disadvantage
  - EI versus ECNI
  - Elution of interfering compounds
  - Different GC-columns
  - Internal standards

Advantages and Disadvantages

	GC/LR-ECNI-MS	GC/LR-EI-MS	GC/HRMS	LC-MS/MS
LOD	30 fg - 1.7 pg*	0.5 - 32 pg*	0.1 - 4.8 pg*	12 - 30 pg*
Sensitivity	+ +	−	+	− −
Selectivity	No	yes	yes	yes
Labeled standards	No (only for BDE209)	yes	yes	yes
Thermal degradation	yes	yes	yes	no
Expensive	+ −	−	+ +	+
Expert training	−	−	+ +	+
Libary search	No	yes	yes	No
	*Eljarrat et al, (2002) J Mass Spectrom 37: 76-84	*Eljarrat et al, (2002) J Mass Spectrom 37: 76-84	*Alaee et al, (2001) Chemosphere 44: 1489-1495	*Abdallah et al, (2009) Anal. Chem., 81, 7460–7467

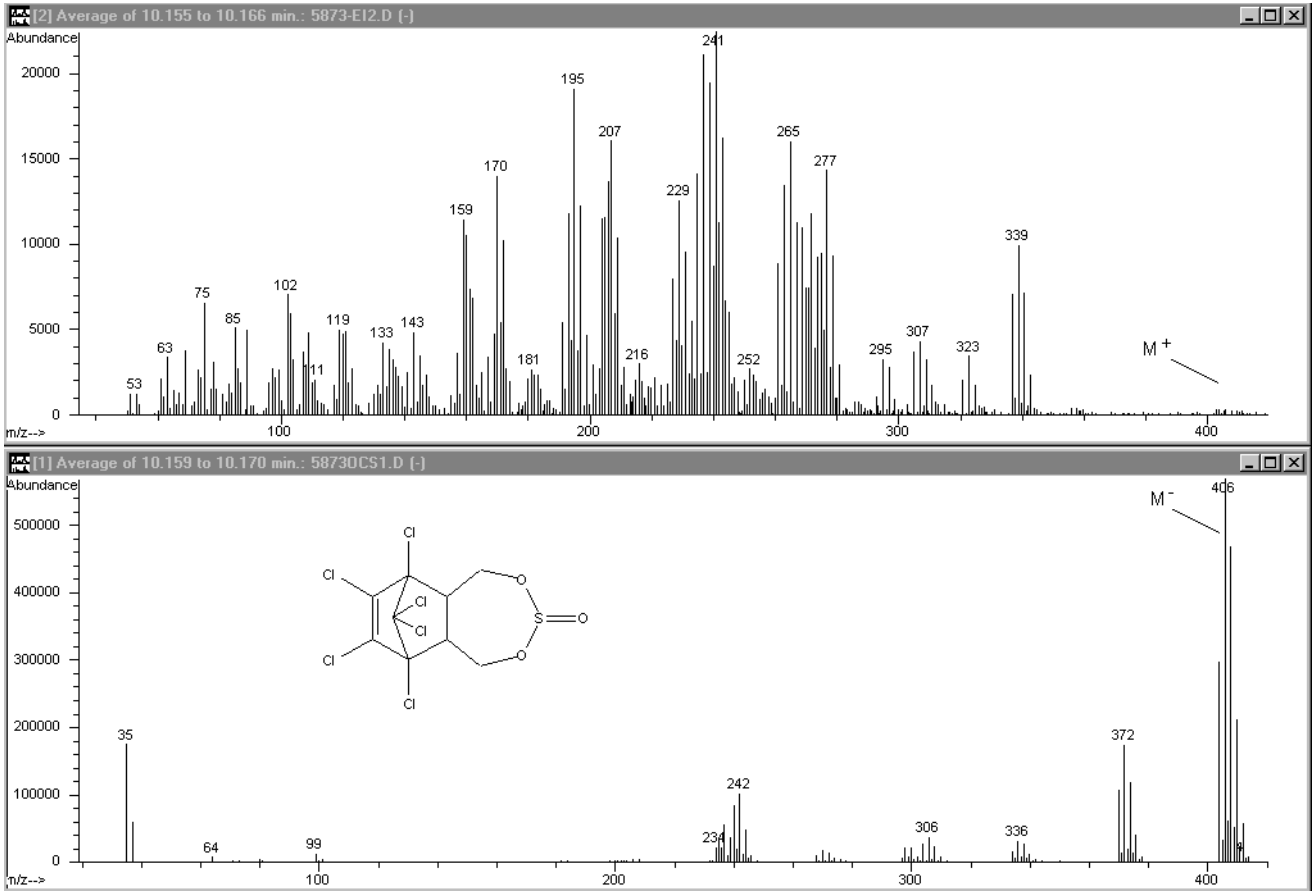

Anal Bioanal Chem (2006) 386: 807–817
DOI 10.1007/s00216-006-0400-y

REVIEW

Heather M. Stapleton

Instrumental methods and challenges in quantifying polybrominated diphenyl ethers in environmental extracts: a review

GC-EI MS versus GC-ECNI MS



Mass spectrum of endosulfan (C9H6Cl6O3S, m. wt. 406 g/mole, CAS number 115-29-7) in EI (upper panel) and ECNI (lower panel). EI produces extensive fragmentation with very little molecular ion formed (M+), but the molecular anion (M–) is the most abundant peak in ECNI. The fragment at 372 *m/z* is formed by loss of chlorine which also appears at 35 and 37 *m/z.*

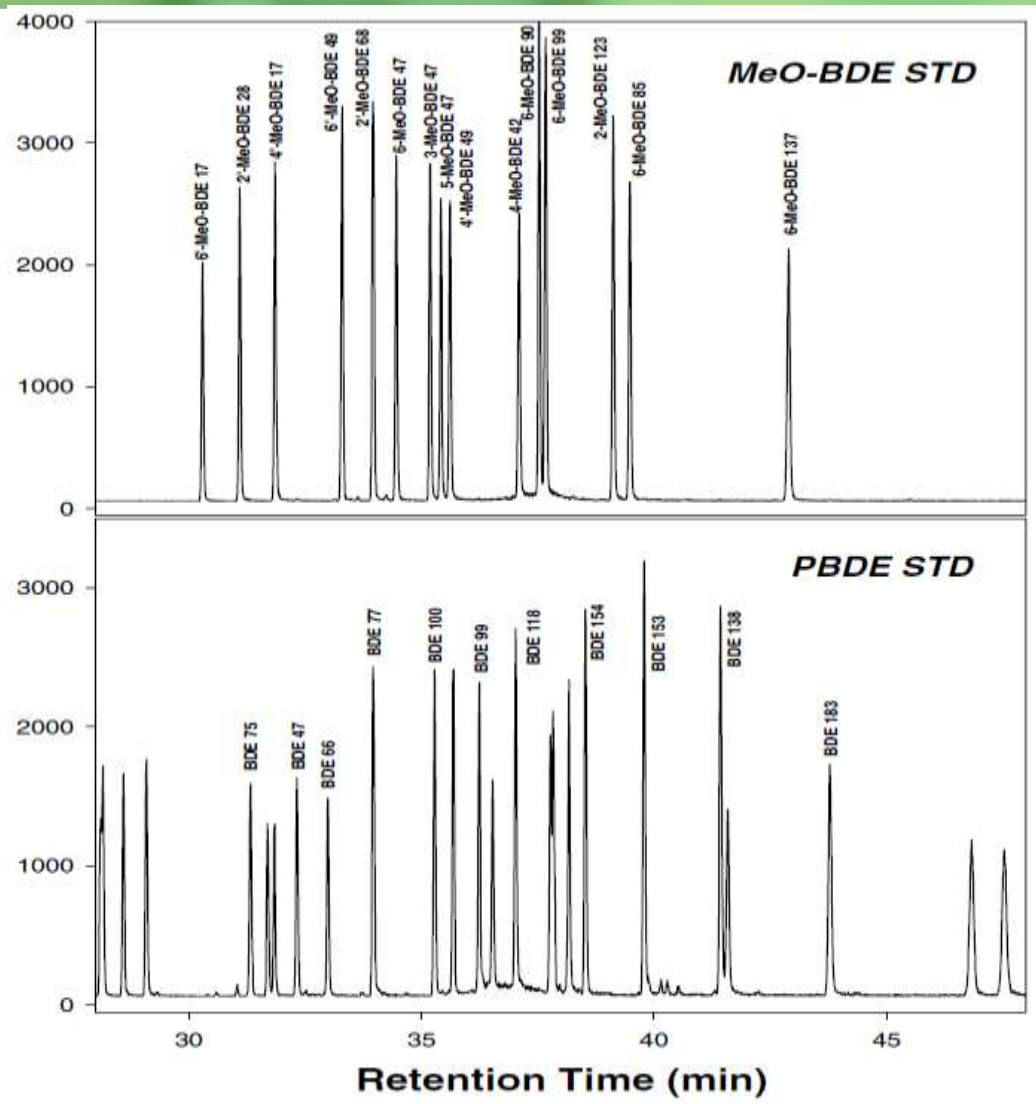
Interfering compounds

•PBBs: BB-153 may interfere with BDE-154 when ECNI-MS is applied.

•TBBPA may interfere with BDE-153 when ECNI-MS is applied.

•MeO-PBDEs: 5-Cl-6-MeO-BDE47 and 6'-Cl-2'-MeO-BDE68 may interfere with BDE-99 when ECNI-MS is applied.

•DiMeO-PBDE: 2',6-DiMeO-BDE68 may interfere with BDE-99 when ECNI-MS is applied.



Resolving power of seven different GC- columns

This database is useful for determining the most suitable column for quantitative, congener-specific PBDE analysis.

Column	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
Dimension (m × mm × μm)	30 × 0.25 × 0.25	30 × 0.25 × 0.25	30 × 0.25 × 0.10	30 × 0.25 × 0.25	30 × 0.25 × 0.25	25 × 0.22 × 0.25	17 × 0.15 × 0.30
Number of coeluting BDEs	62	63	66	67	56	62	72
Number of coelutions with flame retardants	24	26	27	30	22	26	29
Co-elution with major BDE congeners							
Major BDE							
28	16, 33	16, 33	16, 33, 38			16, 33, 38	16, 33
47							
49	68, 80	68	68	62	42, 48, 68, 71	68	51, 75
85				155			114
99			116	127			
100			109	101		109, 120	
138			166		HBCD		166
153			HBCD	168			
154	MTBBP-A, BB-153	MTBBP-A, BB 153		105		126	BB 153
183	BB 169	BB 169					

MTBBP-A dimethylated tetrabromobisphenol-A, *HBCD* hexabromocyclododecane

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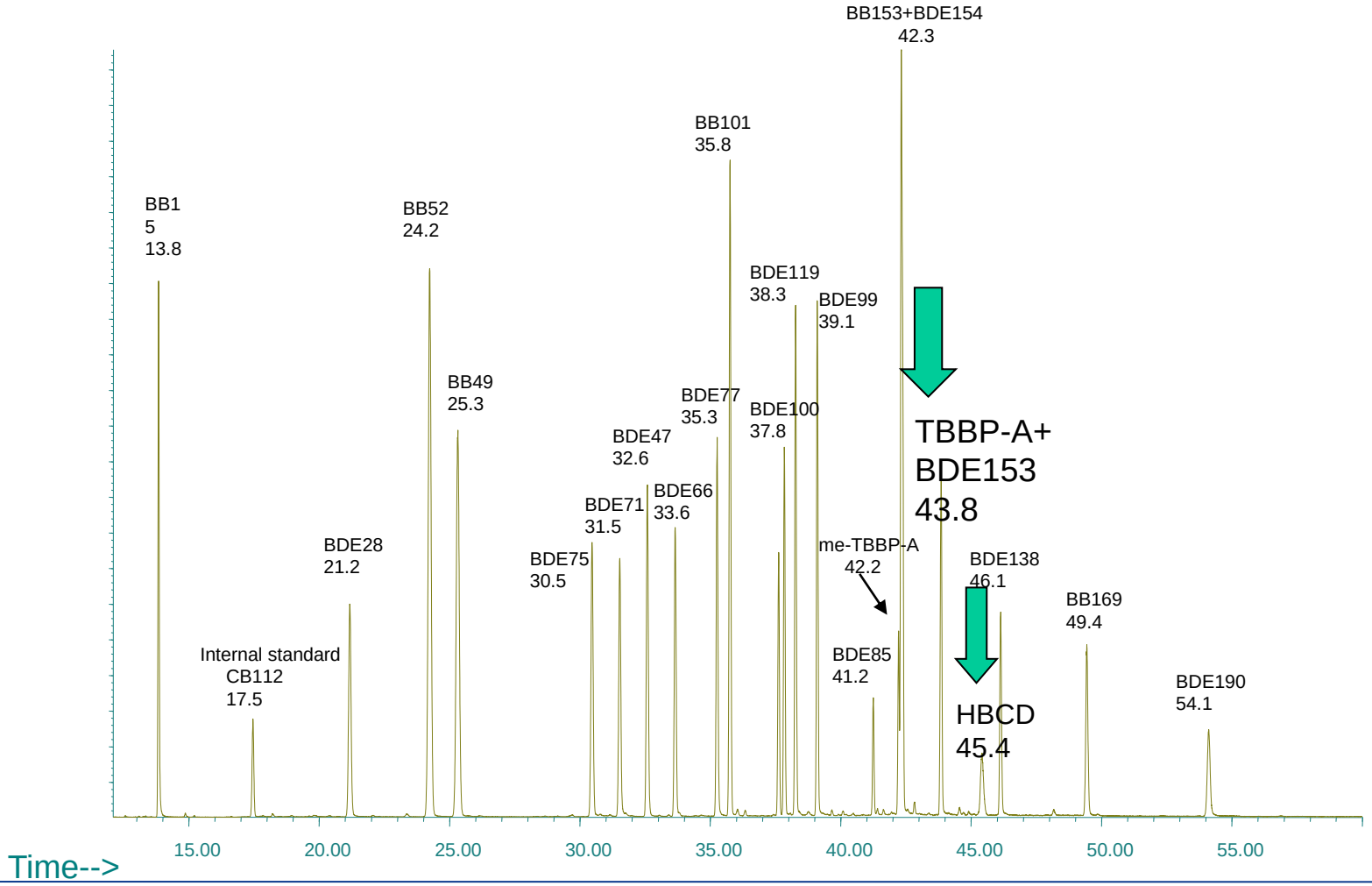
Korytár et al,(2005) J Chromatogr A 1065:239–249

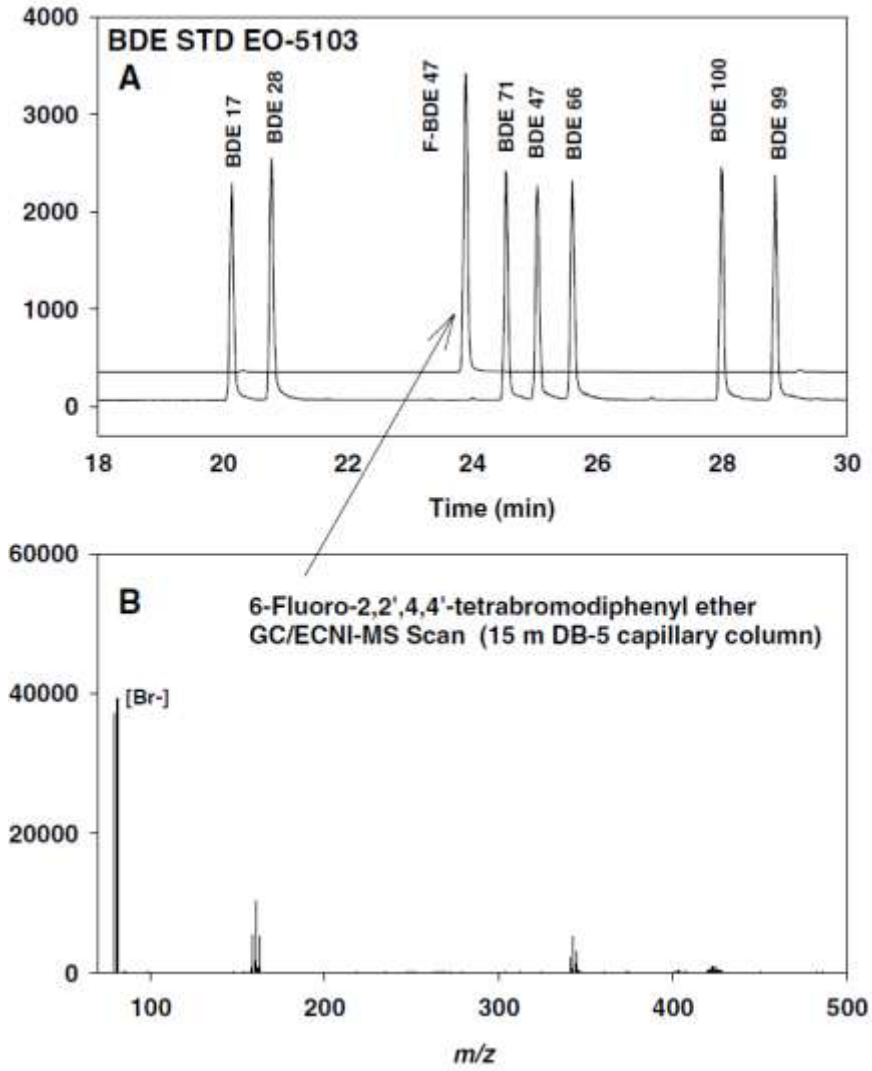
GC-ECNI MS chromatogram

CP-Sil8 CB MS 50 m x 0.25 mm x 0.25 µm



Internal standards

- Internal std for GC-ECNI-MS
  - BDE58
  - BDE77
  - BDE128
  - 13C12 BDE209
  - F-PBDEs

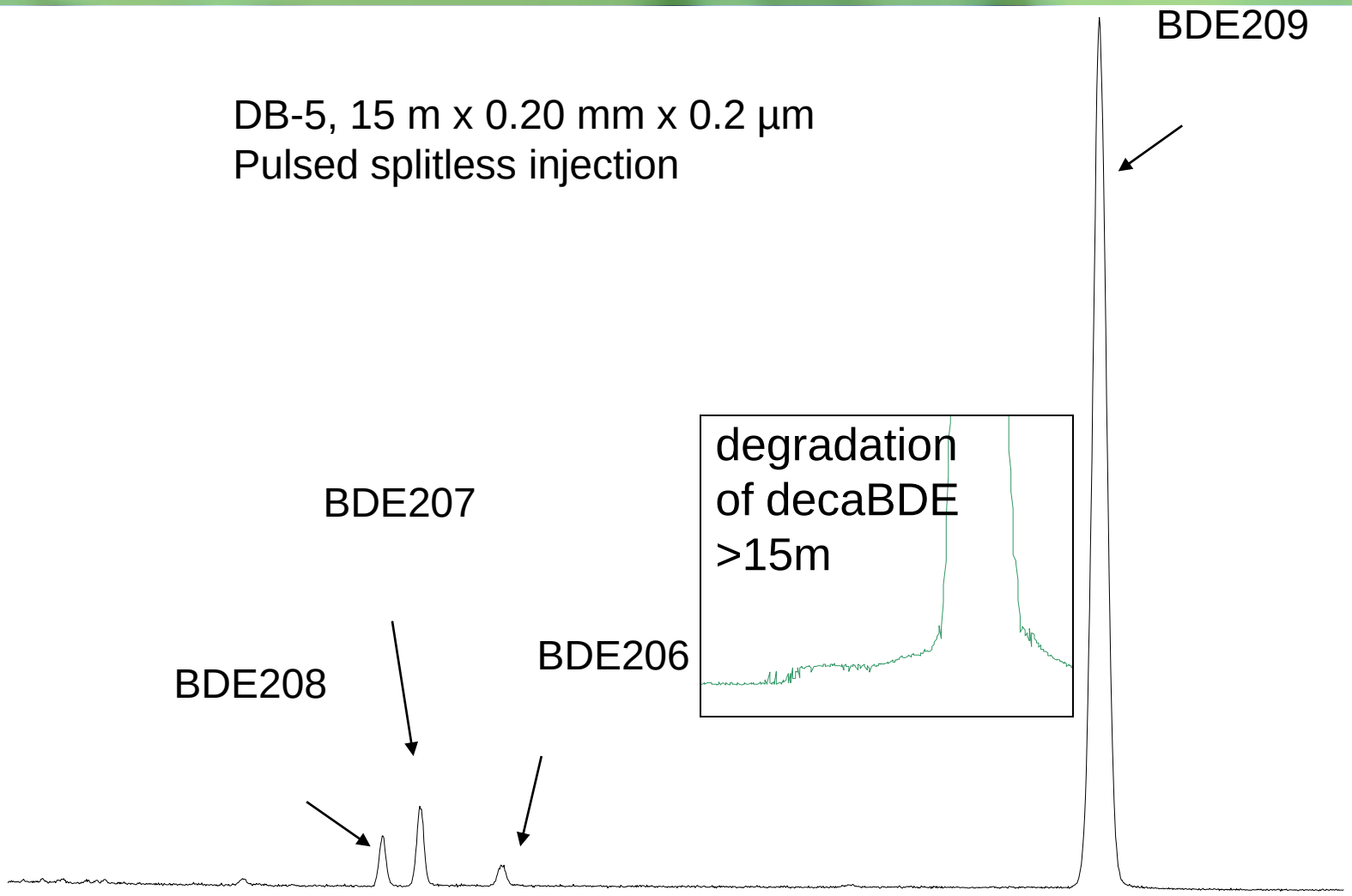


Conclusions

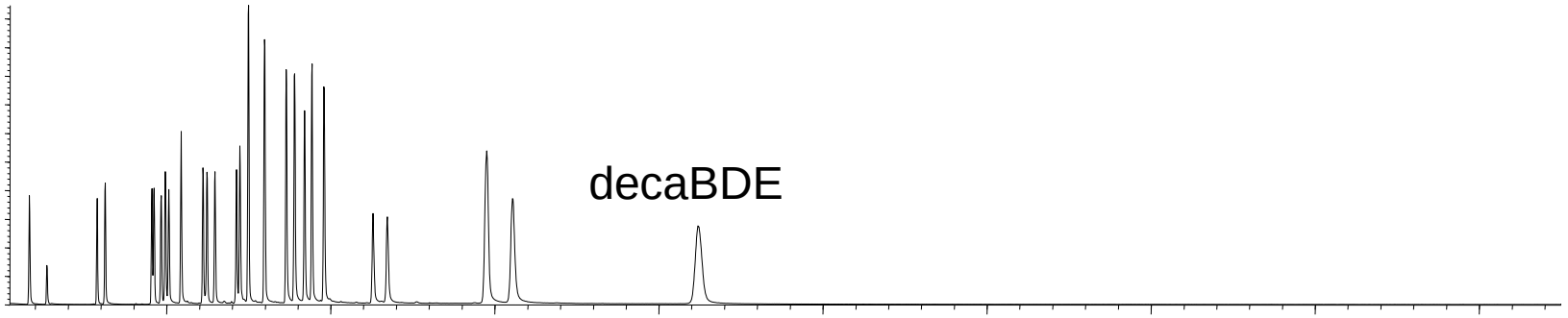
- GC-ECNI-MS is the best all-round method to analyze PBDEs
- Be aware of coeluting of “new” brominated compounds (only measuring m/z 79 and 81 in ECNI mode)
- However when higher detection limits are not a problem GC-EI-MS or LC-MS/MS are good alternatives
- Advantage of EI over ECNI mode is the use of labelled internal standards

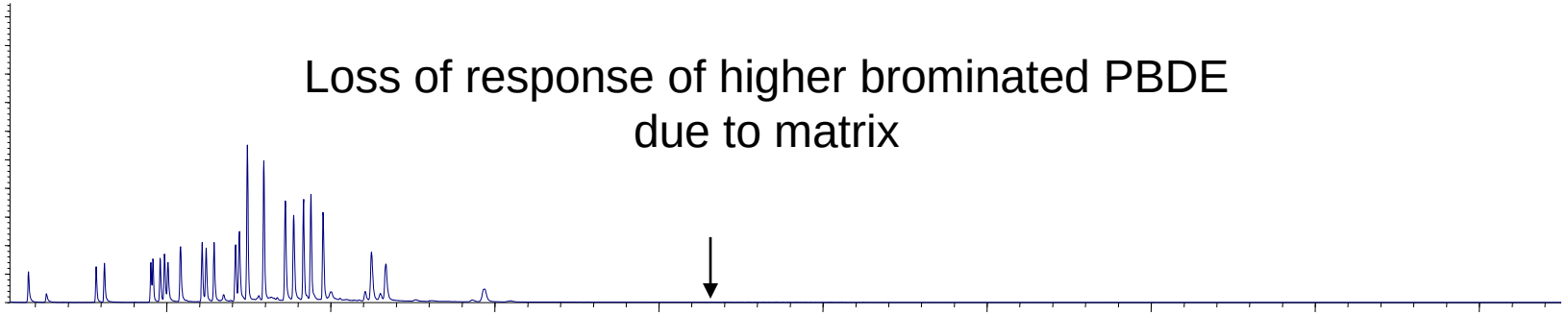
BDE209

BDE209 GC/ECNI-MS

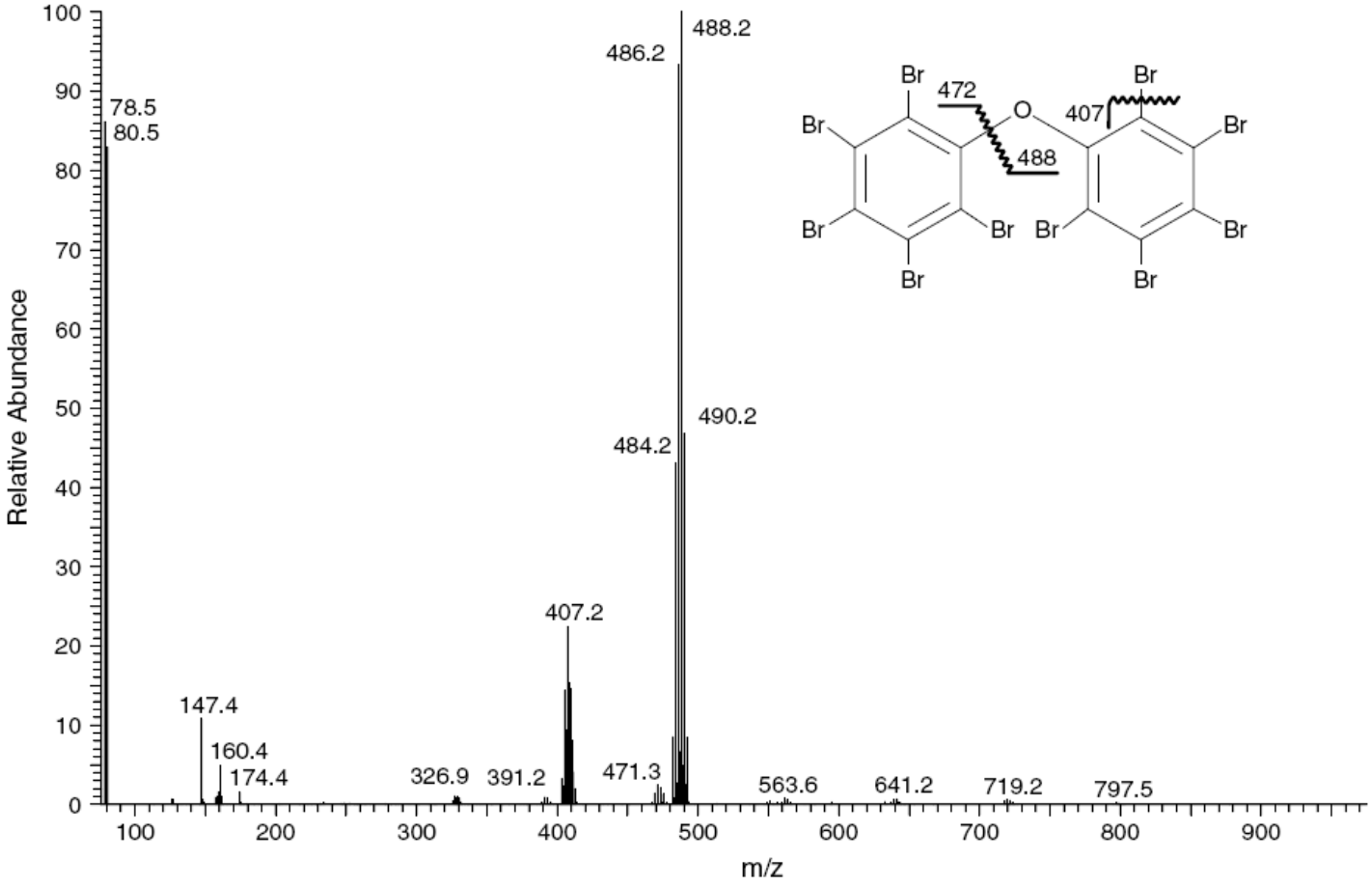


Matrix effects

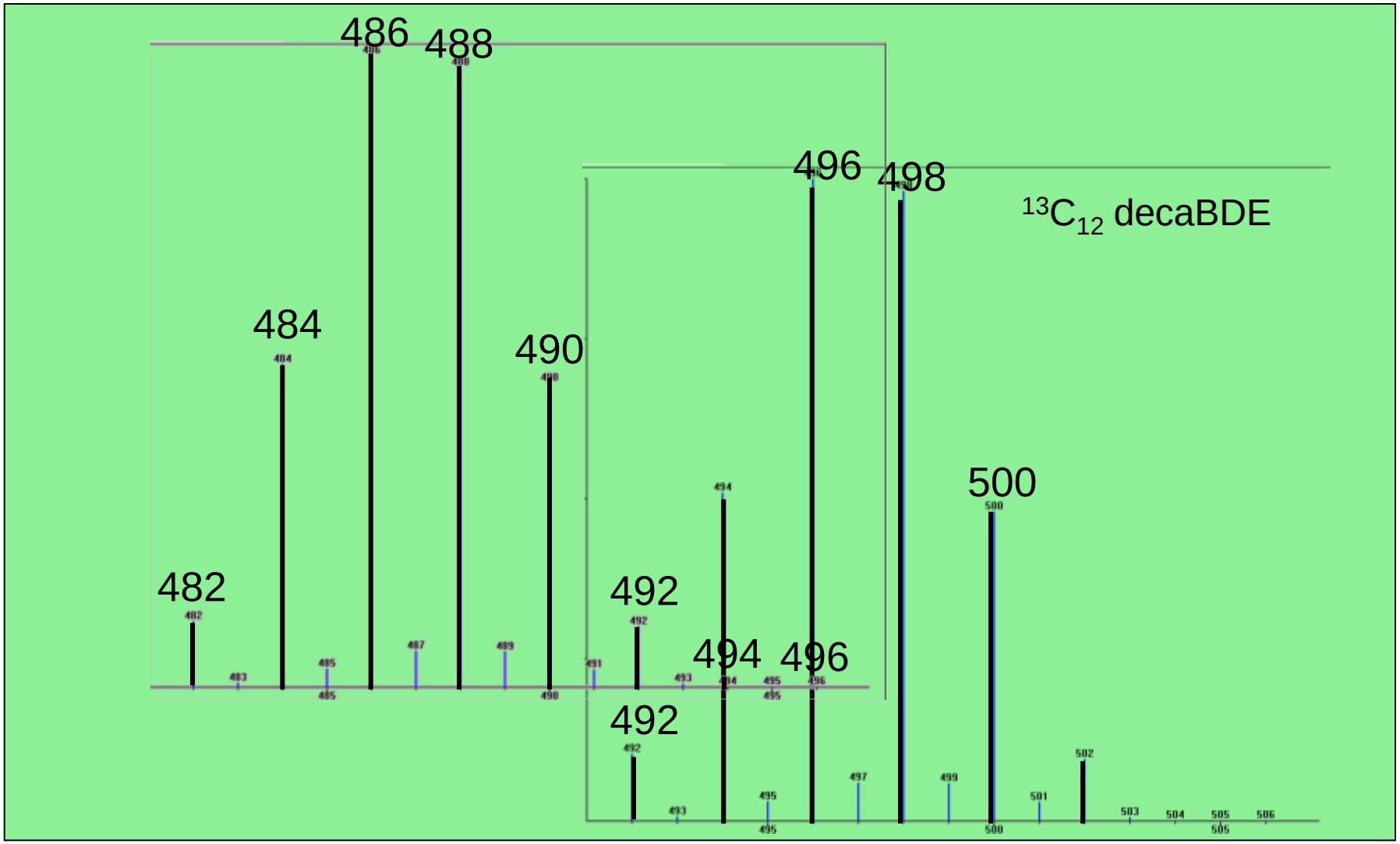




MS spectra (ECNI) of BDE209



MS spectra (ECNI) of $^{13}C_{12}$ BDE209



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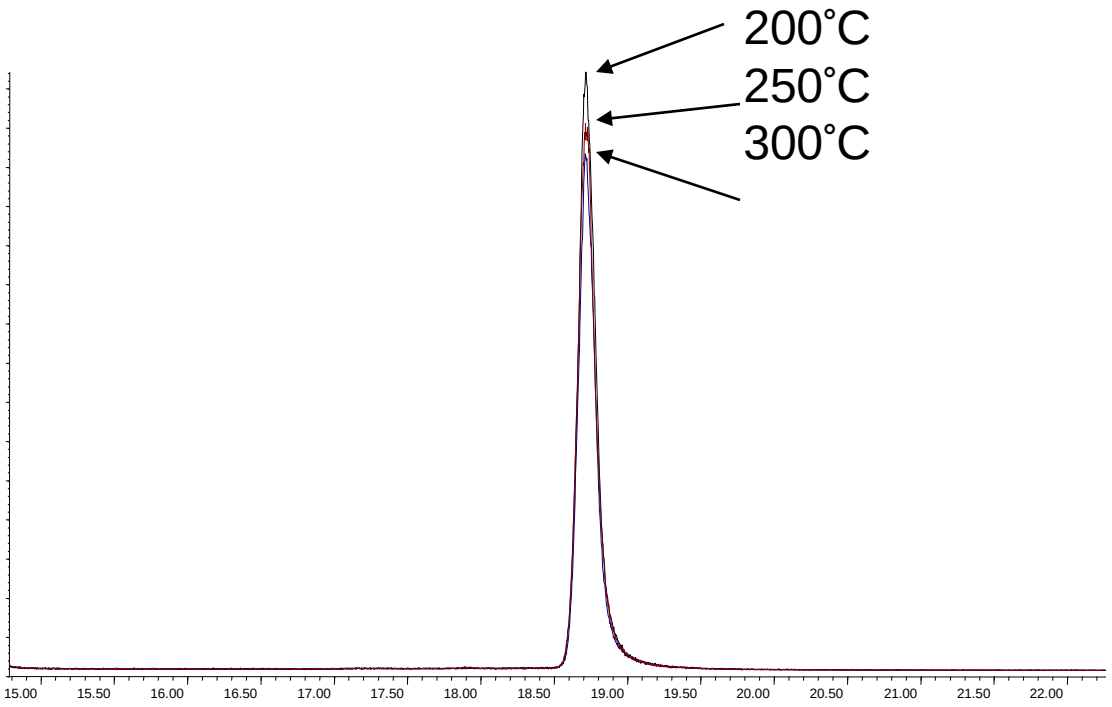
Bjorklund et al, 2003 J. Mass Spectrom. 38, 394-400

Ion source (ECNI) temperature



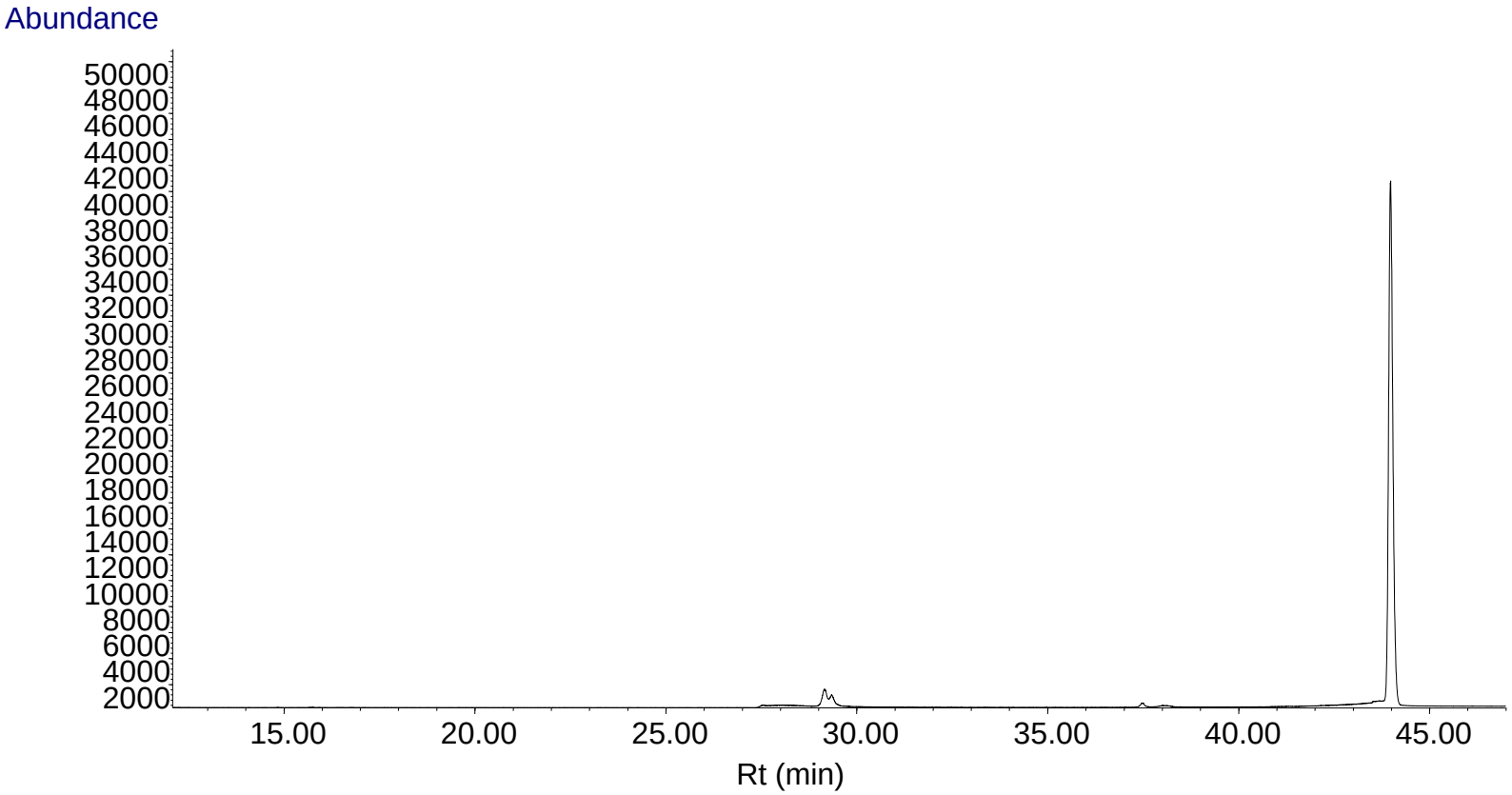
Summary for BDE209

- Use 13C decaBDE as internal standard
- Use <15 m GC column
- Use short injector residence times (pulsed splitless) or on-column injection
- Reduce sample exposure to glassware and reduce if possible number of pieces of glassware used
- If possible physically segregate sample by type and analysis in separate areas
- Reduce UV-light exposure (UV-filters or amber glassware)
- Reduce and avoid dust

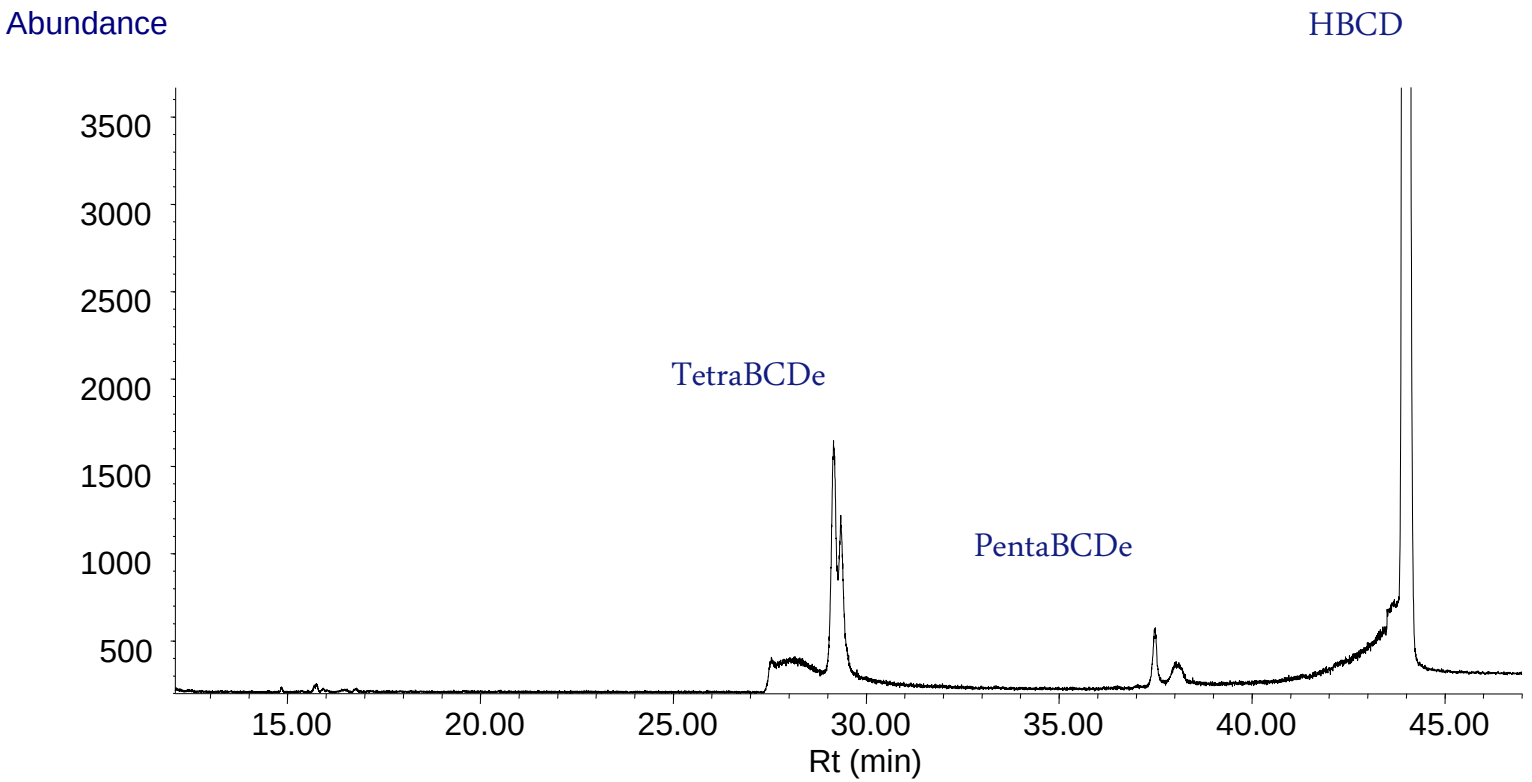
HBCD

GC or LC ?

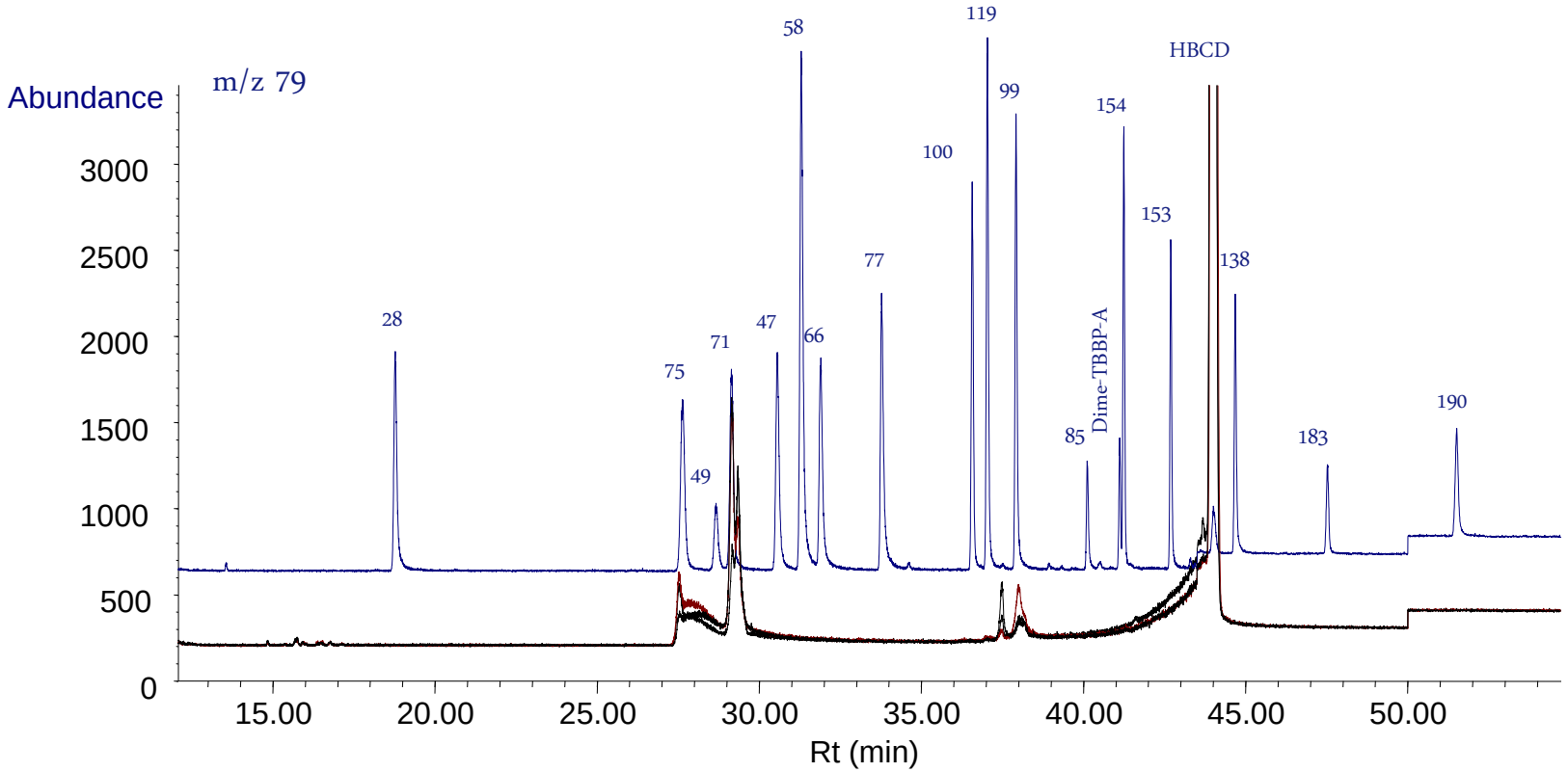
GC-MS (ECNI) HBCD (I)



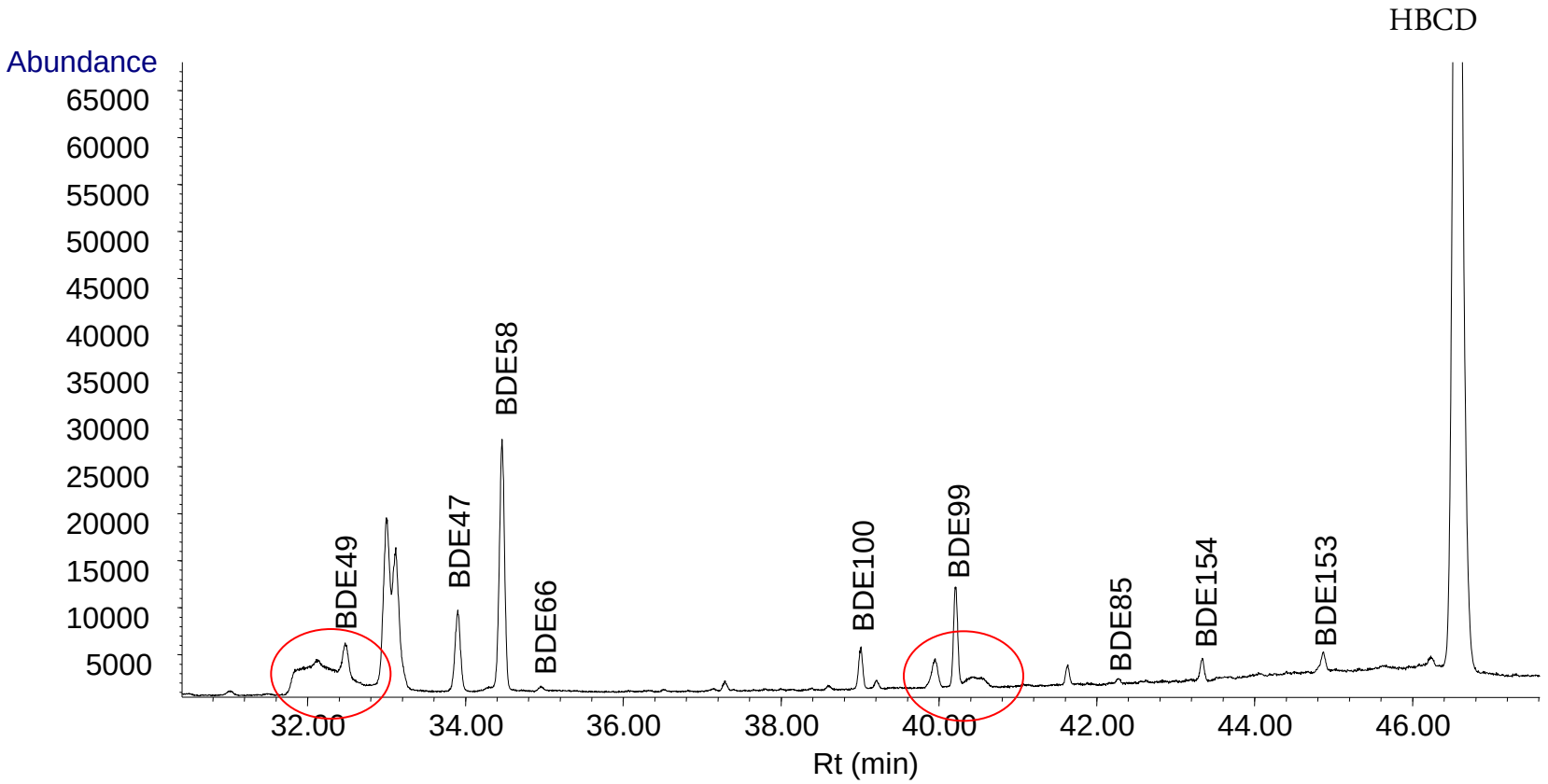
GC-MS (ECNI) HBCD (II)



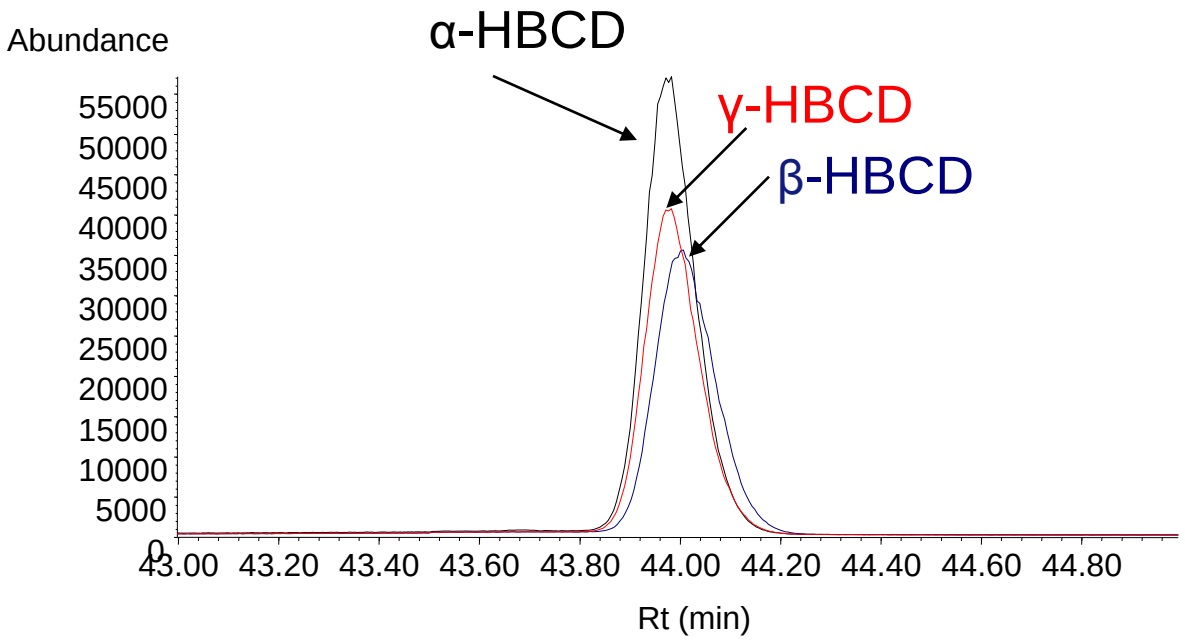
GC-MS (ECNI) HBCD and PBDEs



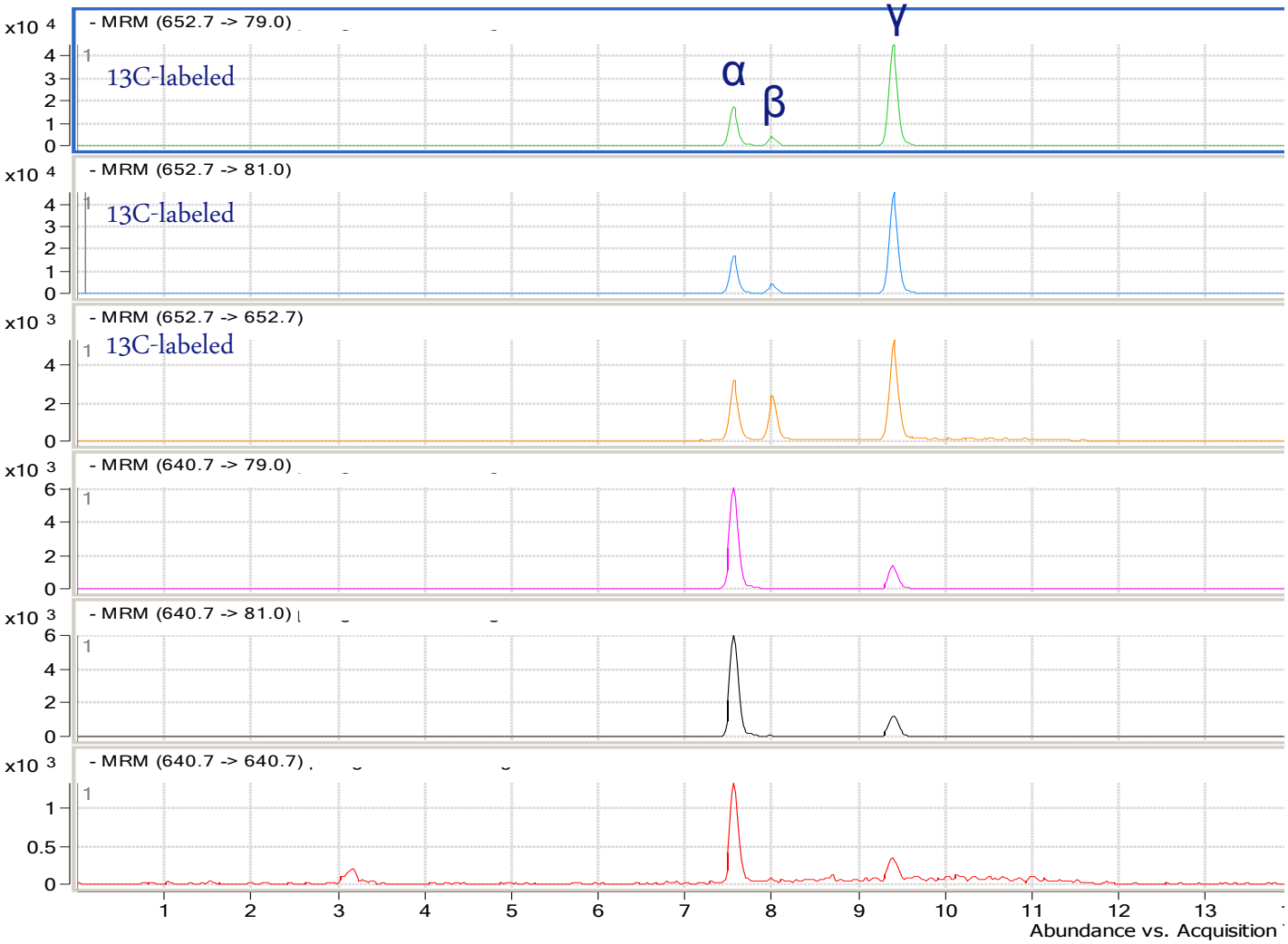
Sediment sample, Scheldt estuary



GC-MS ECNI response HBCD isomers

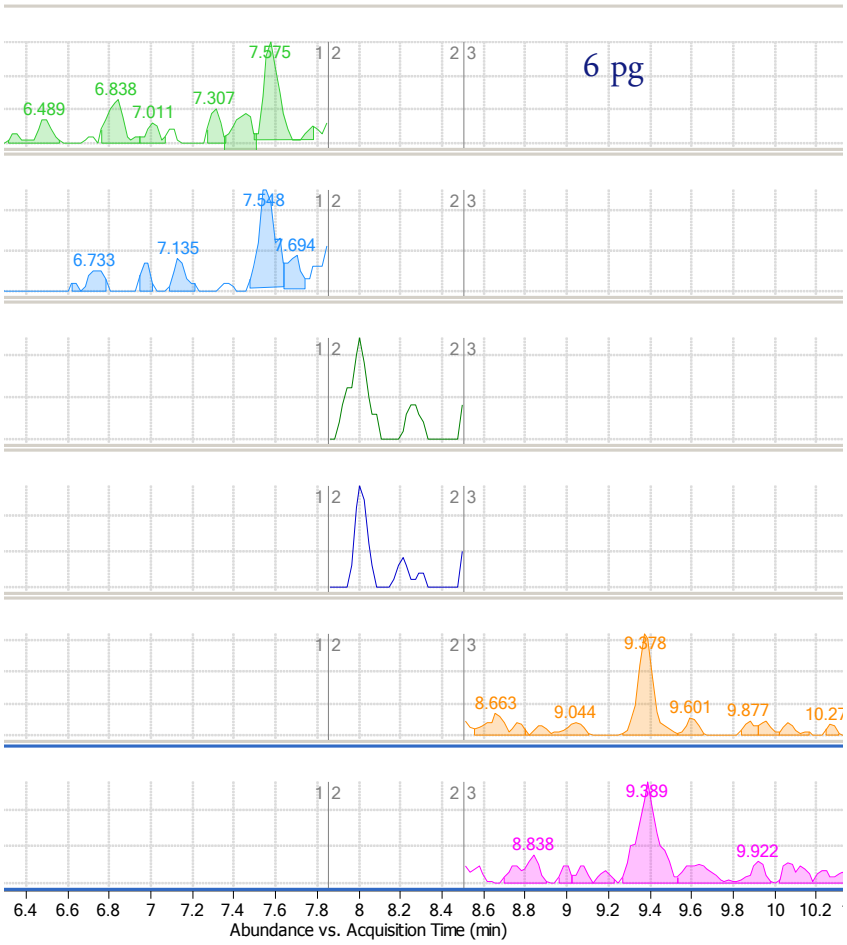


Eel, LC-MS/MS, HBCD

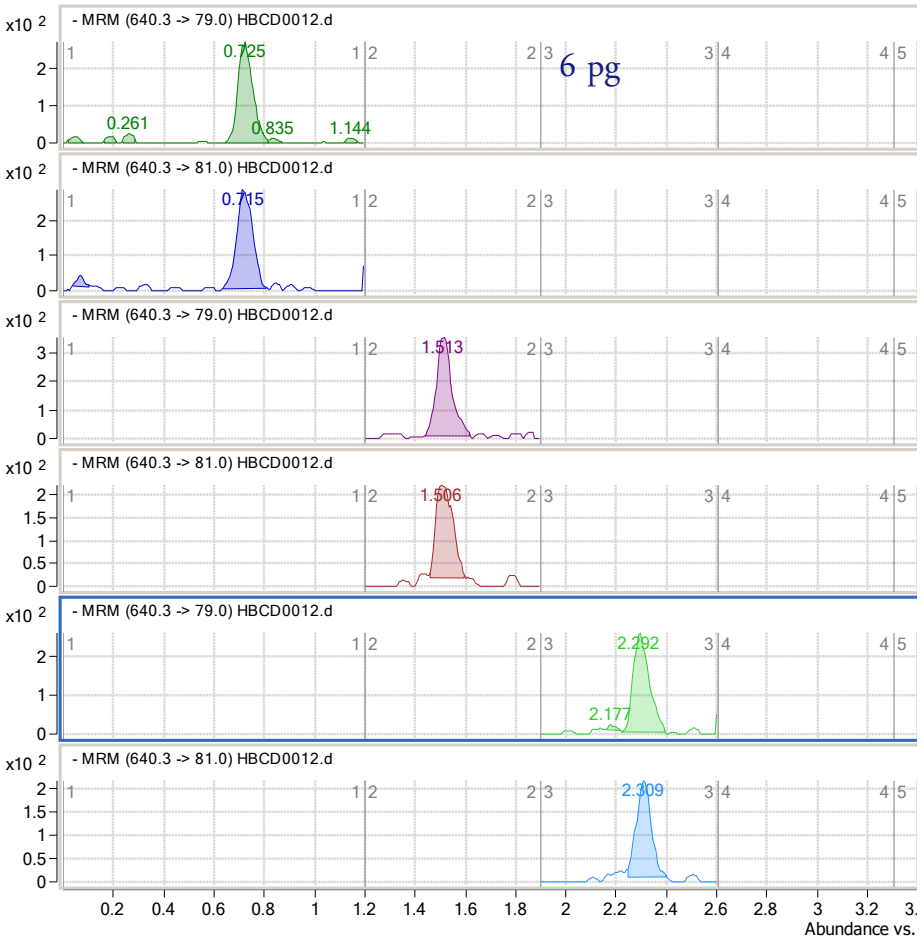


Normal LC vs. Rapid Resolution LC columns

Zorbax Eclips, 2.1 x 150 mm x 3.5 um



Zorbax SB-C18, 2.1 x 30 mm x 3.5 um



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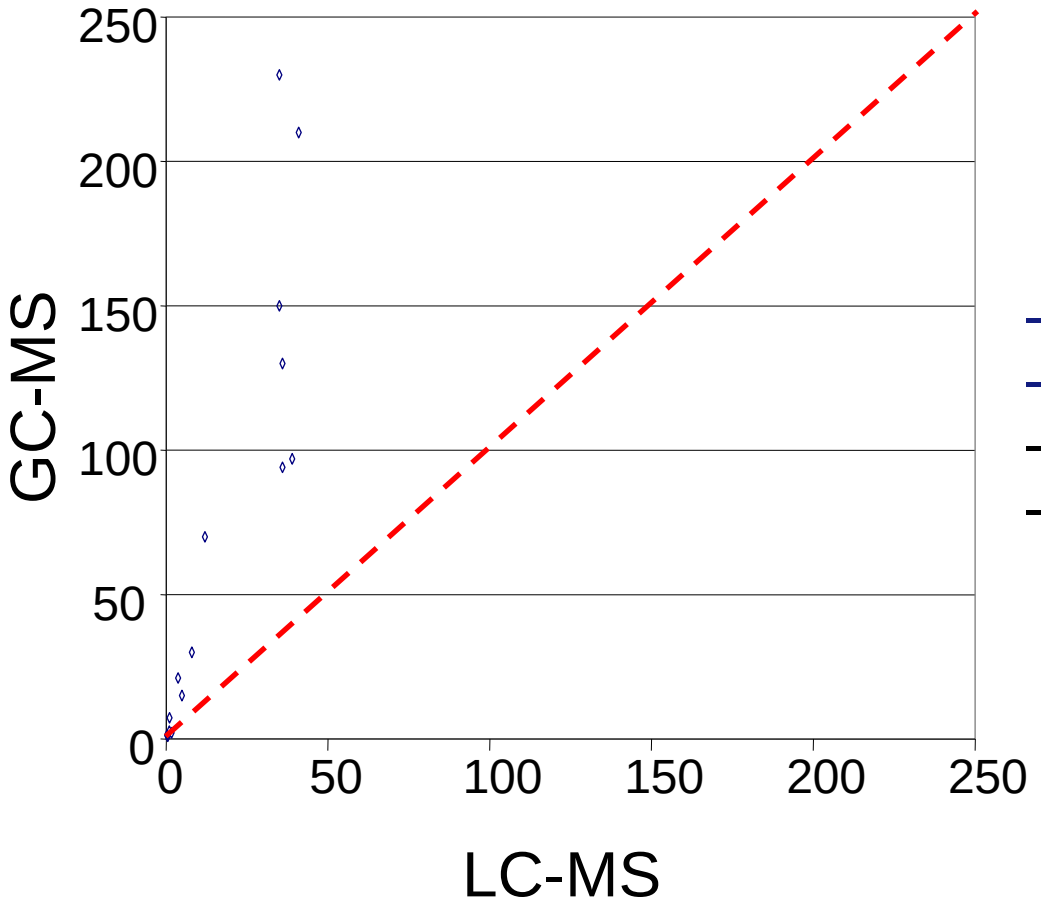
Quantification of HBCD: LC vs. GC

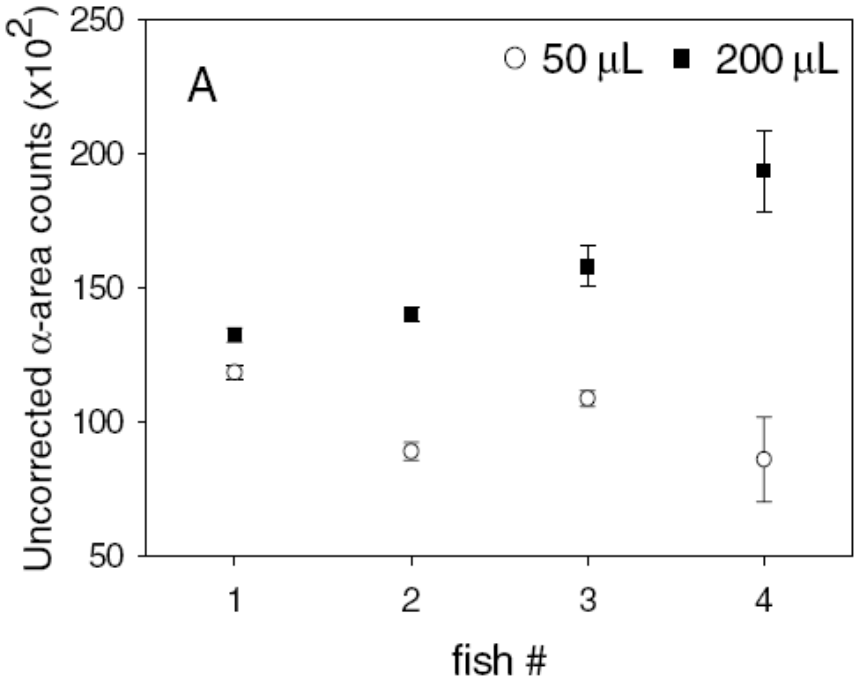


-GC: internal standard conc. (no ^{13}C)
-GC: response factors isomers differ
-isomers transferred into each other
-LC: Ion-suppression

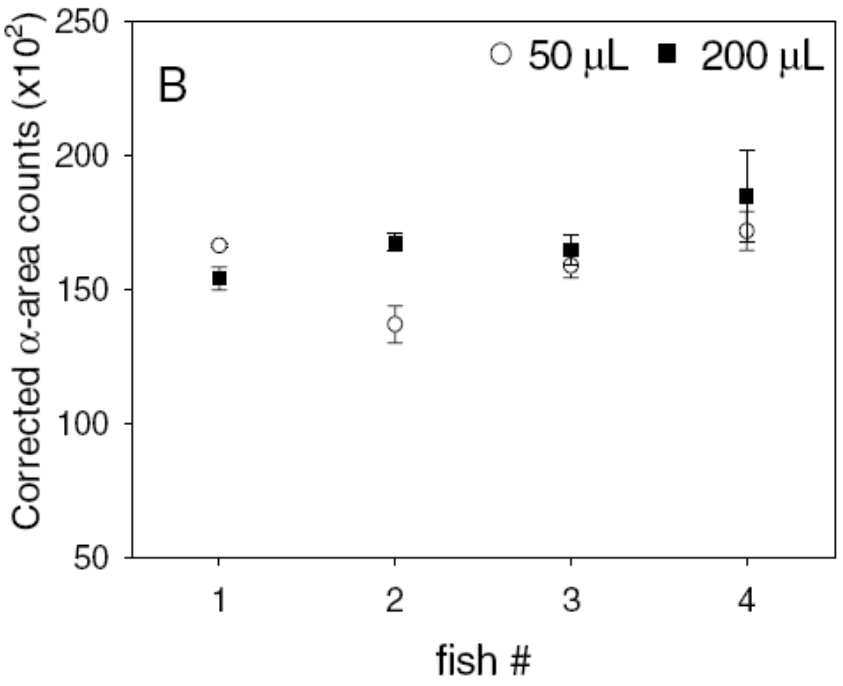
Ion suppression of HBCD signal by matrix compound

LC-MS/MS

Uncorrected



Corrected, 13C-labelled



Tomy et al. 2005, Rapid Comm. Mass Spectr. 19, 2819-2826

Conclusions

HBCD

- GC: Thermal degradation on GC column
- Thermal degradation causes interfering peaks with PBDEs
- LC-MS preferred method
- Use of 13C-labeled IS is preferred
- LC-MS/MS (1 pg) as sensitive as GC-MS (0.5 pg)

TBBP-A

GC or LC ?

GC-MS TBBP-A

- Without derivatization poor calibration curves
- Interference TBBP-A and BDE153
- With derivatization -> dime-TBBP-A

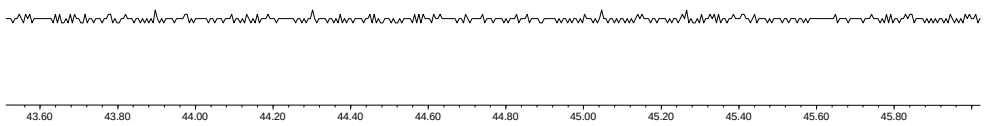
GC-MS TBBP-A

Sediment, Scheldt estuary

TBBP-A standard

10 ng/ml, 1 µl injection

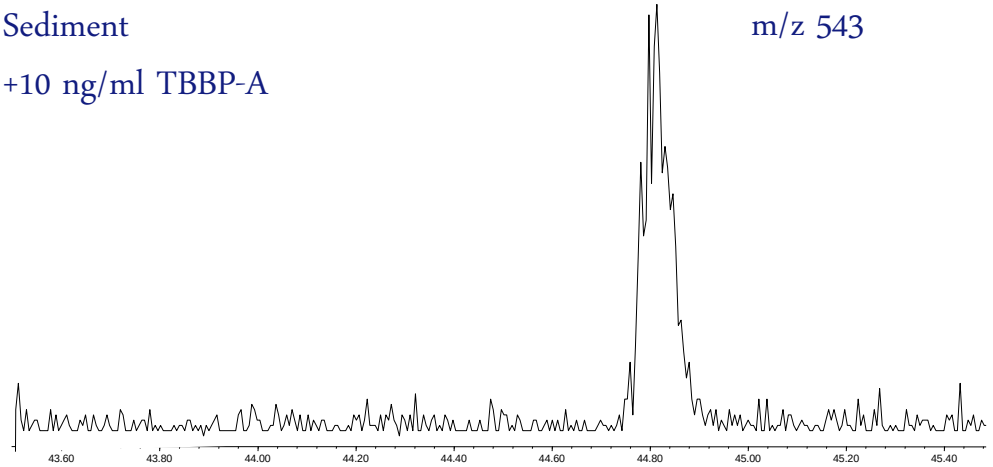
m/z 543



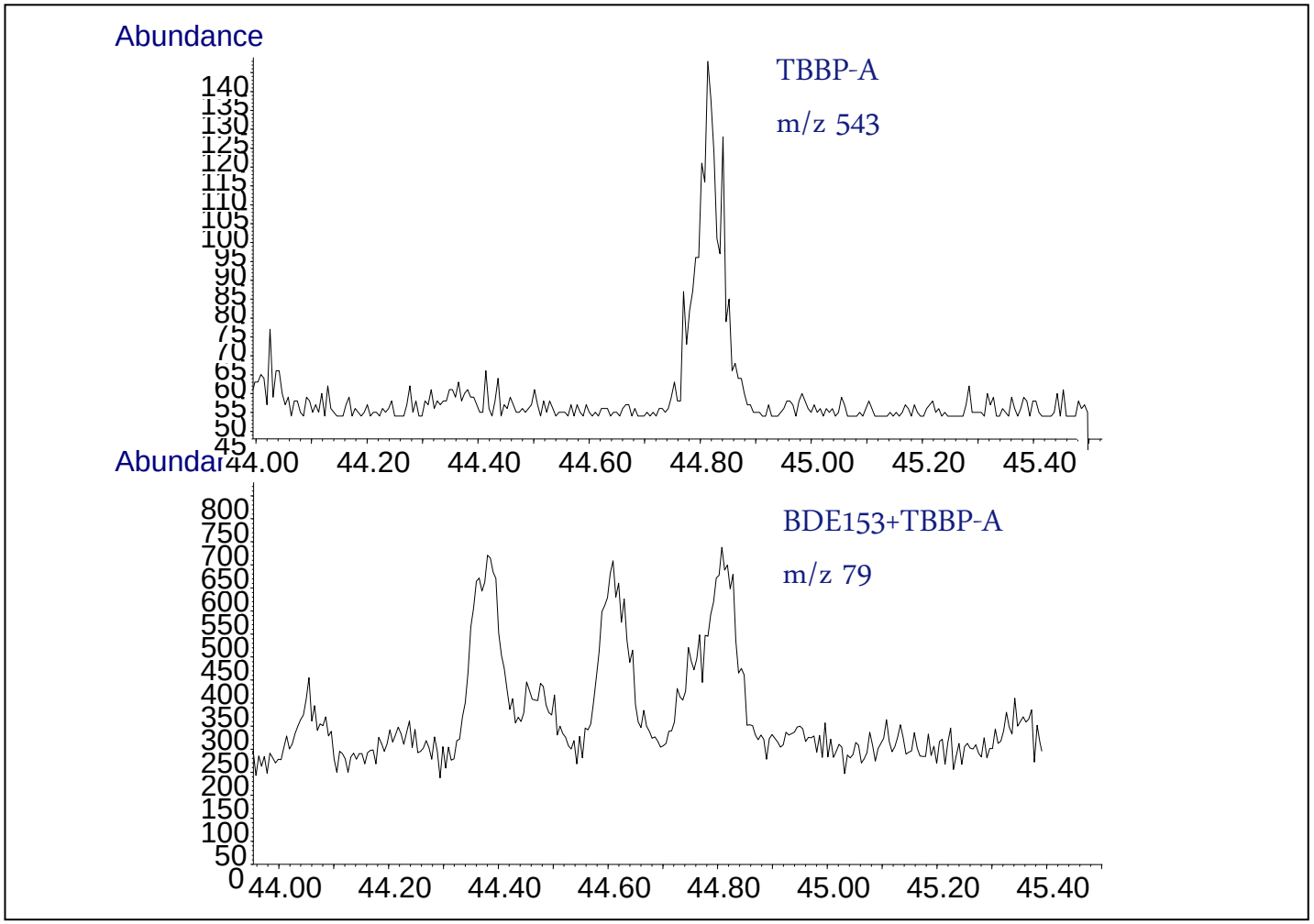
Sediment

+10 ng/ml TBBP-A

m/z 543

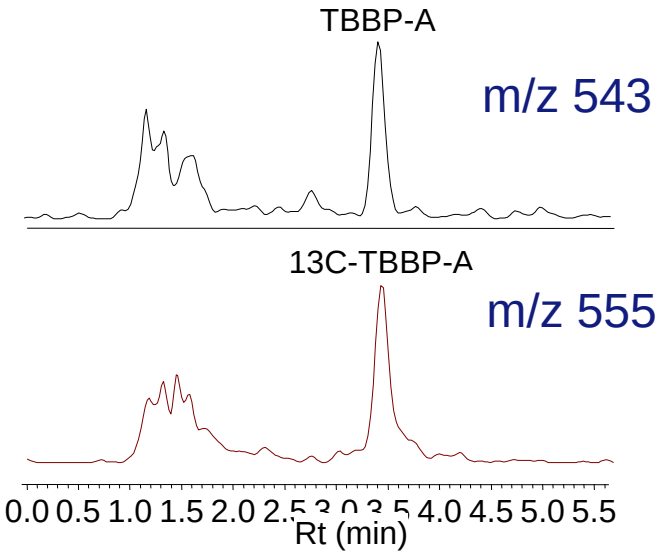


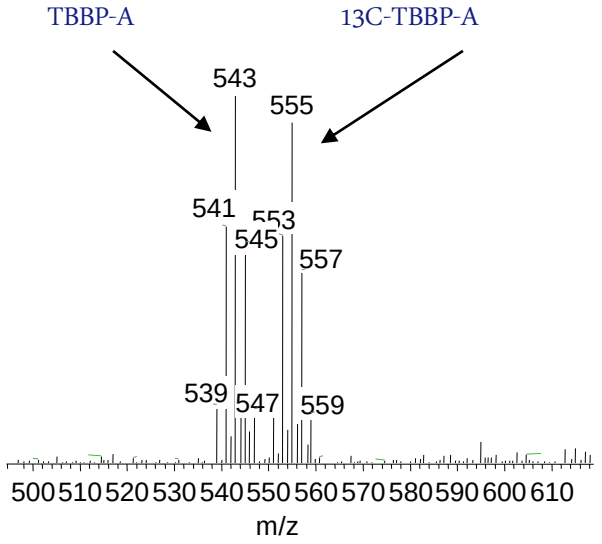
TBBP-A and BDE153



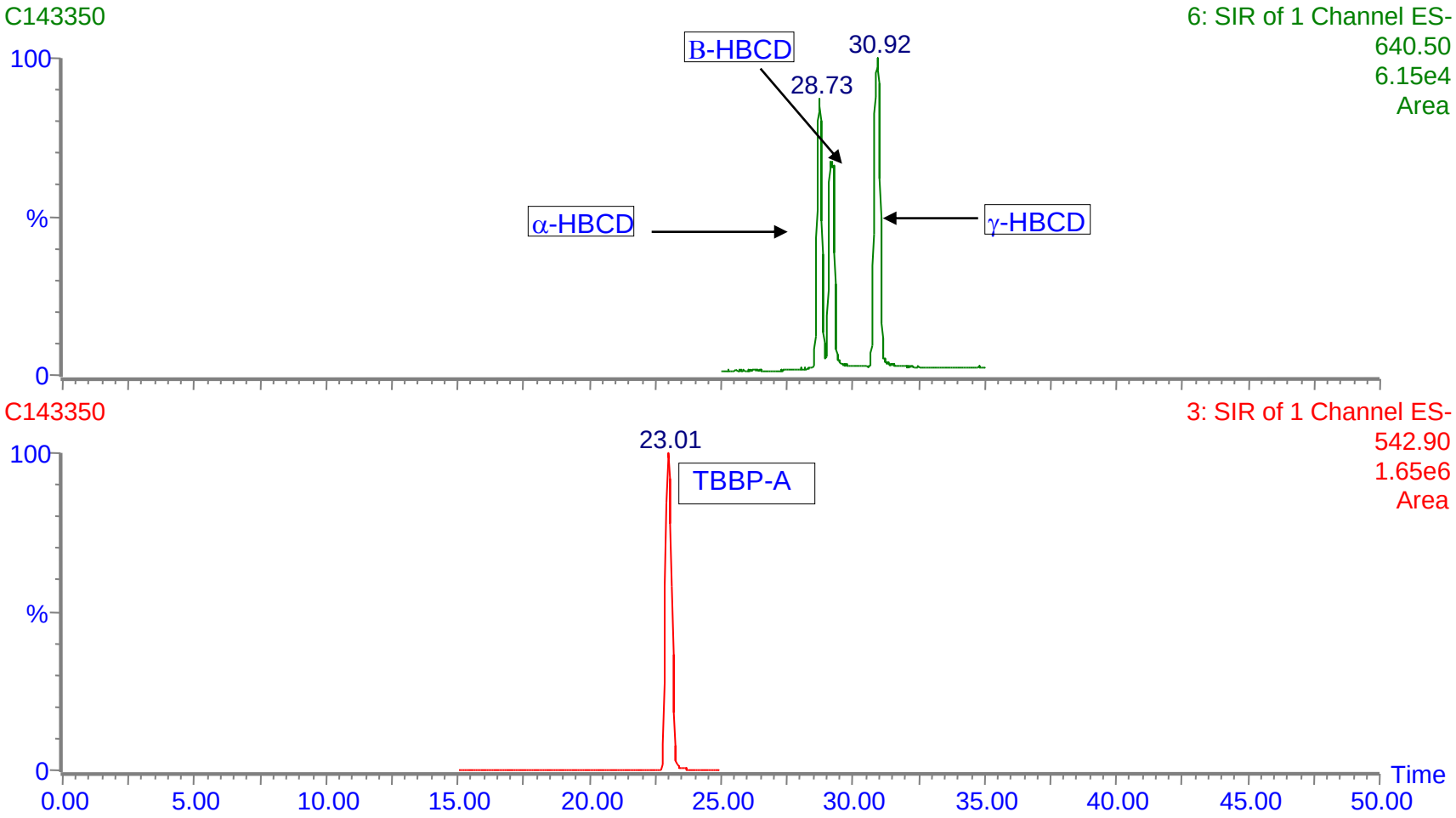
TBBP-A analysis

- LC-MS easy to perform





LC-MS/MS: HBCD and TBBP-A



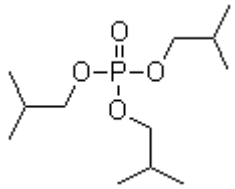
Conclusions

TBBP-A

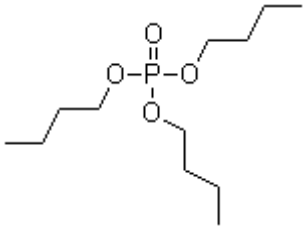
- LC-MS preferred method, use 13C-labelled IS
- GC-MS (ECNI) BDE153 and TBBP-A interfere
- 13C-TBBP-A can cause interference with BDE153
- Sample treatment most critical step

PFRs

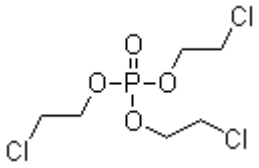
PFRs



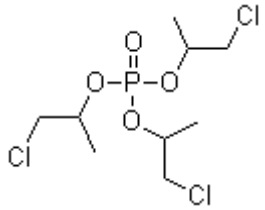
TiBP



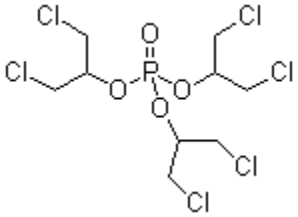
TBP



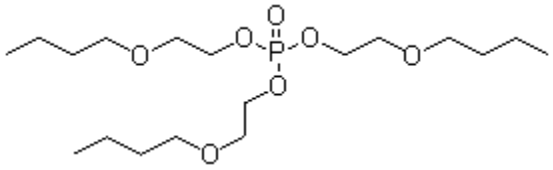
TCEP



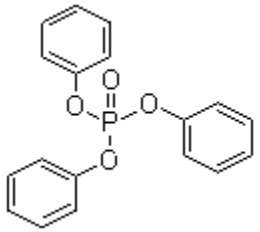
TCPP



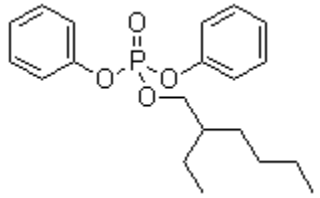
TDCPP



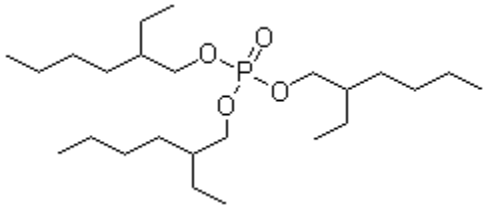
TBEP



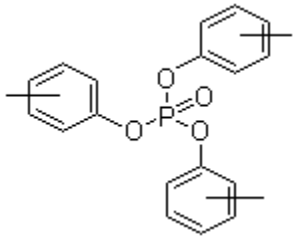
TPP



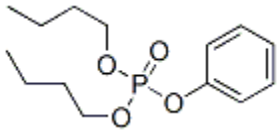
EHDP



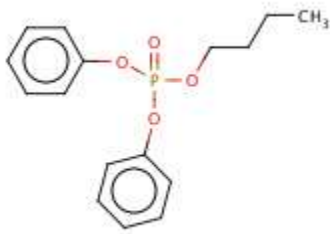
TEHP



TCP



DBPhP



DPhBP

Acronyms, Rt and MRM for twelve PFRs

Compound	Acronym	Retention time	Precursor Ion	Product Ion	Fragmentor	Collision Energy
tri-n-butyl phosphate D27 *	TBP D27	15,8	294.4	166.1	100	15
			294.4	102.1	100	15
tri-n-butyl phosphate	TBP	15,6	267.2	155.1	100	10
			267.2	99.1	100	10
tris(2-chloroethyl) phosphate	TCEP	6,4	287	99.1	100	19
	TCEP		285	63.1	110	18
tris-iso-butyl phosphate	TiBP	15,8	267.2	155.1	75	8
			267.2	99.1	75	8
tris(chloro 2-propyl) phosphate	TCPP	11,6	329	99	100	15
tris(1,3-dichloro-2-propyl)phosphate	TDCPP	14,4	433	99.4	125	30
tris(2-butoxyethyl) phosphate	TBEP	16,4	399.4	299.2	125	15
			399.4	199.1	125	15
tris(2-ethylhexyl) phosphate	TEHP	22,8	435.4	113.3	125	10
			435.4	99.1	125	10
triphenyl phosphate d15 *	TPP d15	16,4	342.2	160.2	175	40
			342.2	82.1	175	40
triphenyl phosphate	TPP	14,5	327.2	152.1	175	35
			327.2	77.1	175	35
tricresyl phosphate	TCP	17,1	369.2	165.2	175	35
			369.2	91.1	175	35
2-Ethylhexyl diphenyl phosphate	EHDP	17,5	251.1	152.2	150	28
			251.1	77.2	150	28
Butyl diphenyl phosphate	BDphP	15	307.2	251.1	100	6
Dibutyl phenyl phosphate	DBphP	15,4	287.2	175.1	100	8

HPLC column 150 x 3 mm Luna C18 (2) 3 um column (Phenomenex)

GC/EI-MS

Compound	Abbreviation	Identification–quantification ions	Retention times[a] (min)		Internal standard used
			HT-8	AT-5	
Tri-ethyl-phosphate	TEP	**155**	5.20	4.37	IS 1
Tri-*n*-propyl-phosphate	T*n*PP	**183**	8.73	7.67	IS 1
Tri-*iso*-butyl-phosphate	T*i*BP	155, **211**	10.27	9.34	IS 1
Tri-*n*-butyl-phosphate	T*n*BP	155, **211**	11.98	10.88	IS 1
Tris-(2-chloroethyl)-phosphate	TCEP	251, **249**	13.79	12.14	IS 1
Tris-(2-chloroisopropyl) phosphate	TCPP 1	279, **277**	14.04	12.57	IS 1
(mixture of 3 isomers)[b]	TCPP 2	279, **277**	14.20	12.71	IS 1
Tri-(2-butoxyethyl)-phosphate	TBEP	199, **299**	18.70	18.17	IS 1
Tris-(2,3-dichloropropyl)-phosphate	TDCPP 1	379, **381**	18.81	17.64	IS 2
(mixture of 2 isomers)	TDCPP 2	379, **381**	19.08	17.98	IS 2
Tri-phenyl-phosphate	TPP	325, **326**	19.11	18.14	IS 2
Tri-cresyl-phosphate	TCP 1	367, **368**	20.30	20.09	IS 2
(mixture of 4 isomers)	TCP 2	367, **368**	20.50	20.31	IS 2
	TCP 3	367, **368**	20.71	20.53	IS 2
	TCP 4	367, **368**	20.93	20.76	IS 2
Tri-amyl-phosphate (IS 1)	TAP	169, **239**	14.97	13.82	n.a.
Tri-phenyl-phosphate-d15 (IS 2)	TPP-d15	339, **341**	19.05	18.08	n.a.

n.a. – not applicable.

[a] Retention times on two capillary columns: HT-8 (25 m × 0.22 mm × 0.25 μm) and AT-5 (20 m × 0.18 mm × 0.20 μm).

[b] 3rd isomer not included in calculations.

Van den eede et al, (2011) Environment International 37 454–461

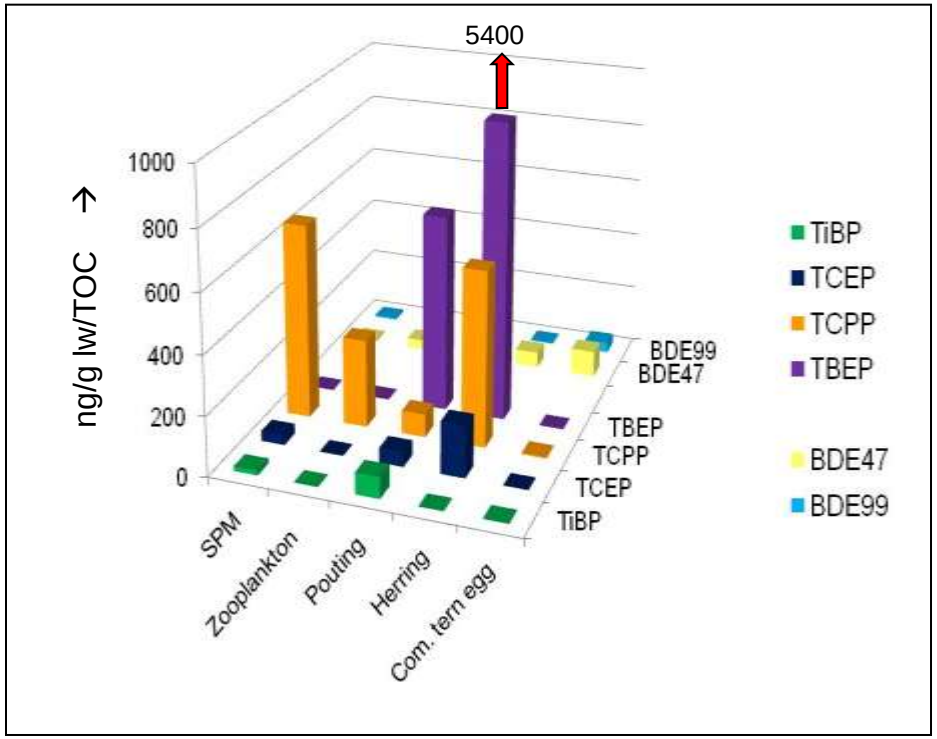
PFRs in Belgian home dust (n=33) µg/g

	House dust samples ($n=33$)				
FRs	DF (%)[a]	Mean	Median	P95[b]	Range
OPFRs					
TEP	0	<0.05	<0.05		
TiBP	100	4.20	2.99	8.81	0.70–15.6
TnBP	100	0.25	0.13	0.63	0.03–2.70
TCEP	86	0.49	0.23	1.72	<0.08–2.65
TCPP	100	4.82	1.38	14.5	0.19–73.7
TBEP	100	6.58	2.03	23.1	0.36–67.6
TPP	100	2.02	0.50	7.28	0.04–29.8
TDCPP	97	0.57	0.36	0.99	<0.08–6.64
TCP	97	0.44	0.24	1.10	<0.04–5.07
∑OPFRs		19.4	13.1	70.3	1.92–94.7
BFRs[c]					
BDE-209	98	0.59	0.31	0.92	<0.001–5.30
∑PBDEs		0.70	0.36	1.14	0.003–6.33
∑HBCDs		1.74	0.13	2.46	0.010–42.70
TBBPA	85	0.04	0.01	0.09	0.002–0.42

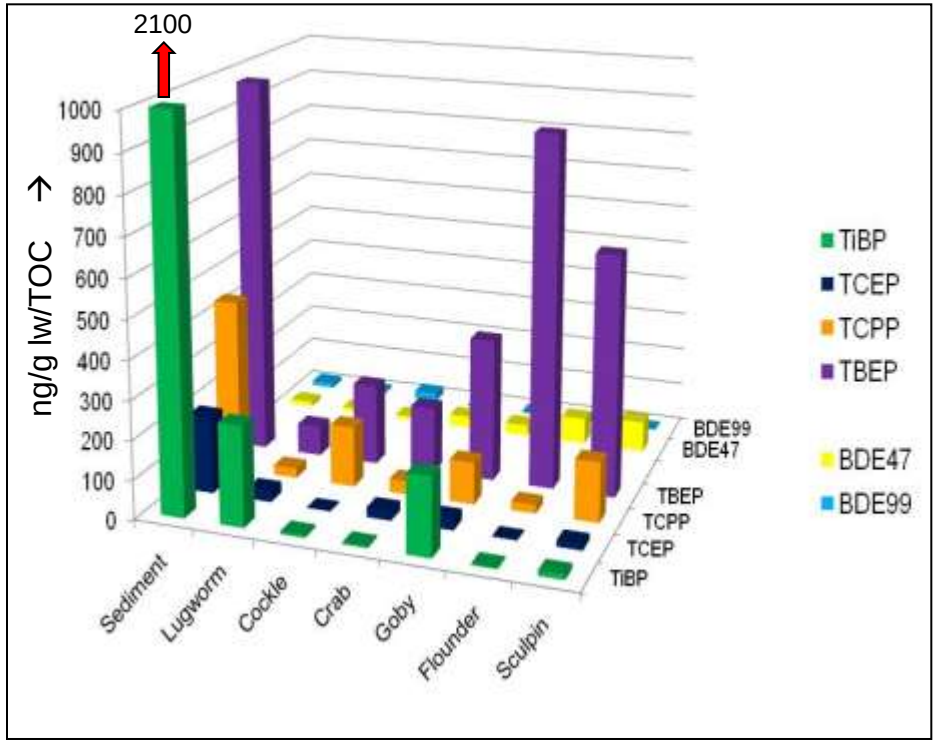
Van den eede et al, (2011) Environment International 37 454–461

Pelagic and Benthic food web

Pelagic food web



Benthic food web



Conclusion

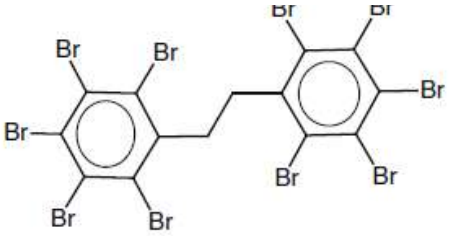
GC or LC

- LC-MS/MS is more selective
- Use of labelled Std
- Less interference of matrices (biota)

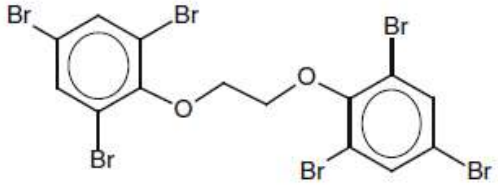
GC/EI-MS

- Good method for analyzing dust (less matrices)
- No ion suppression
- Separation of isomers (TCPP and TCP)

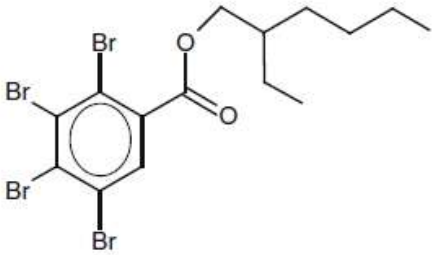
TBB and TBPH
BTBPE and DBDPE



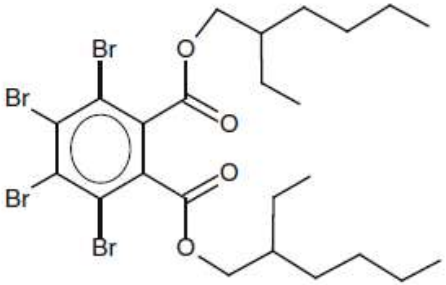
DBDPE



BTBPE



TBB

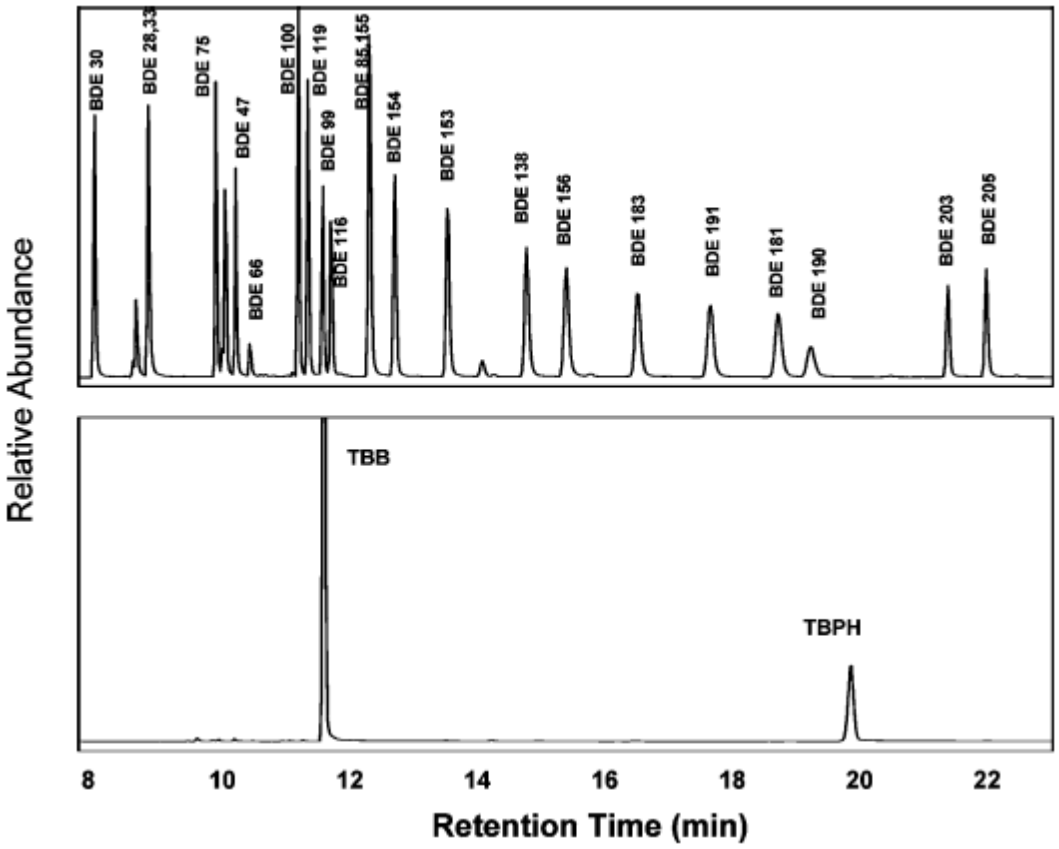


TBPH

Ali et al., (2011) Anal. Bioanal. Chem., **400, 3073-3083**

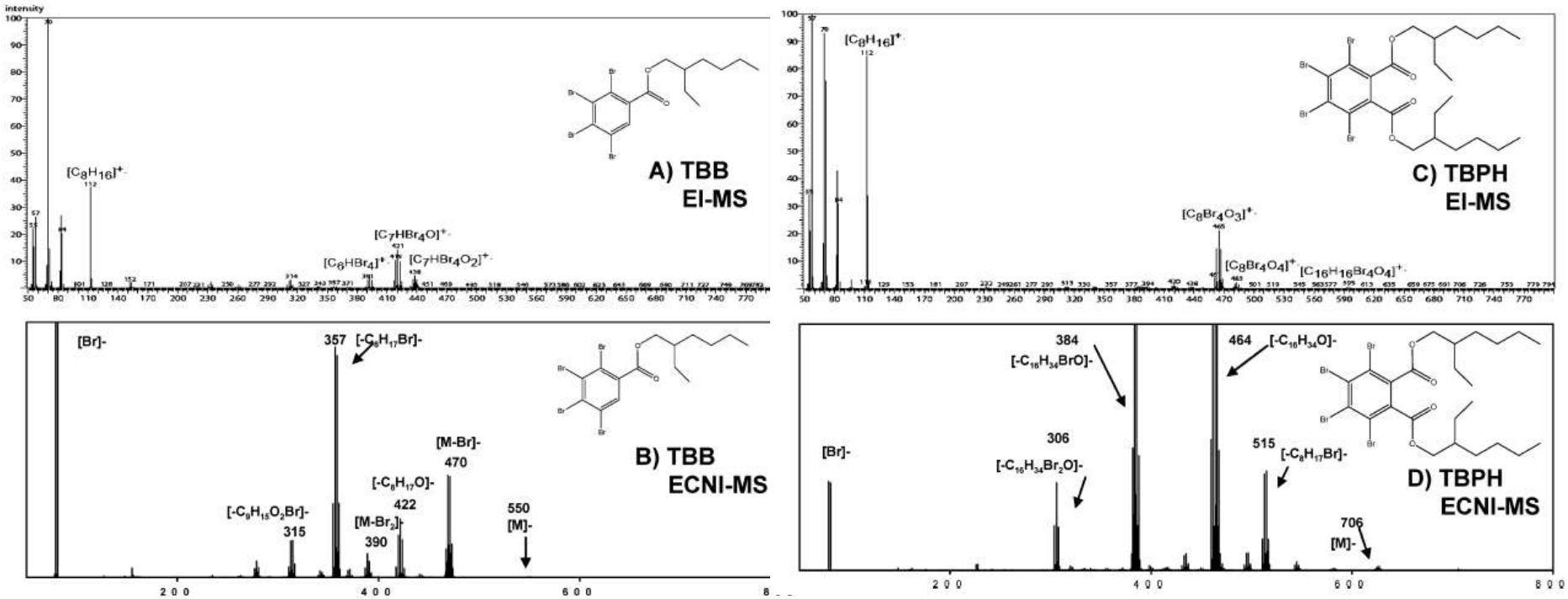
GC/ECNI-MS chromatogram

GC/ECNI-MS chromatograms revealing the relative retention times of the primary BDE congeners, TBB and TBPH on a 15 m DB5-MS column



Stapleton et al, (2008)Environ. Sci. Technol. ***42, 6910–6916***

Full scan spectra of TBB and TBPH



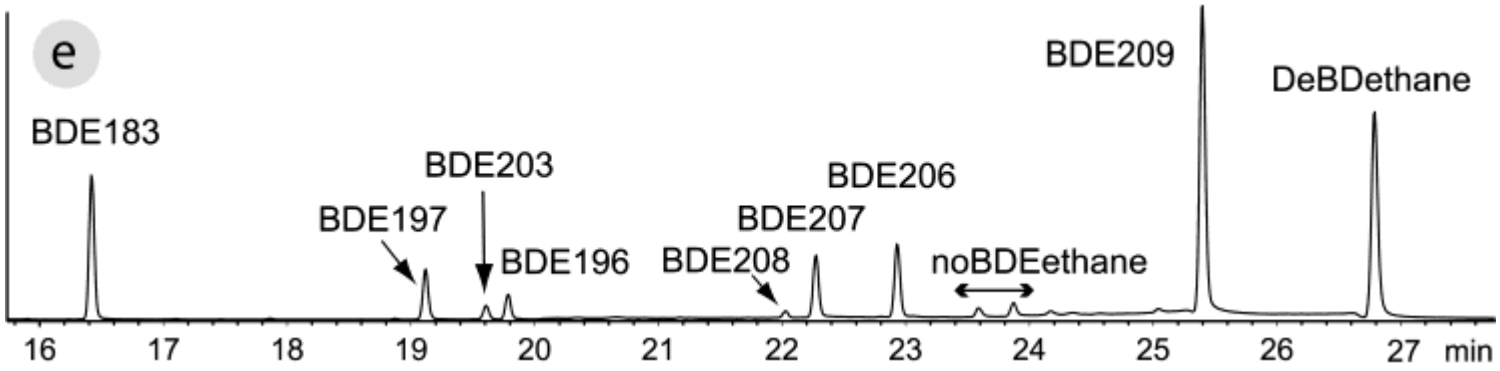
TBB was quantified using ion fragment (*m/z) 357 (Quant)*and 471 (Qual)

TBPH was quantified using ionfragments (*m/z) 463 (Quant) and 515 (Qual)*

Stapleton et al, (2008)Environ. Sci. Technol. ***42, 6910–6916***

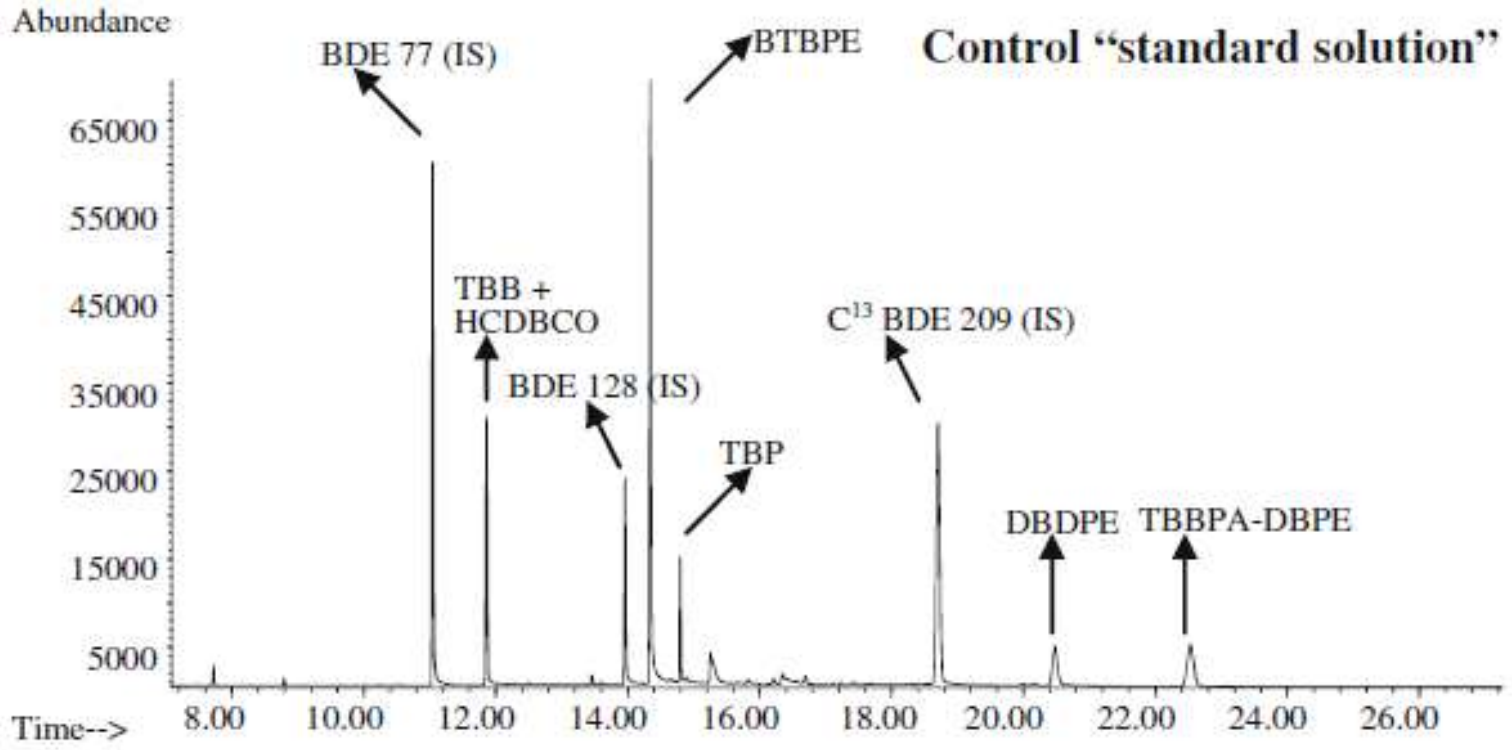
DBDPE first detected in the environment

GC/ECNI-MS chromatogram (m/z 79-+81-) of an standard solution



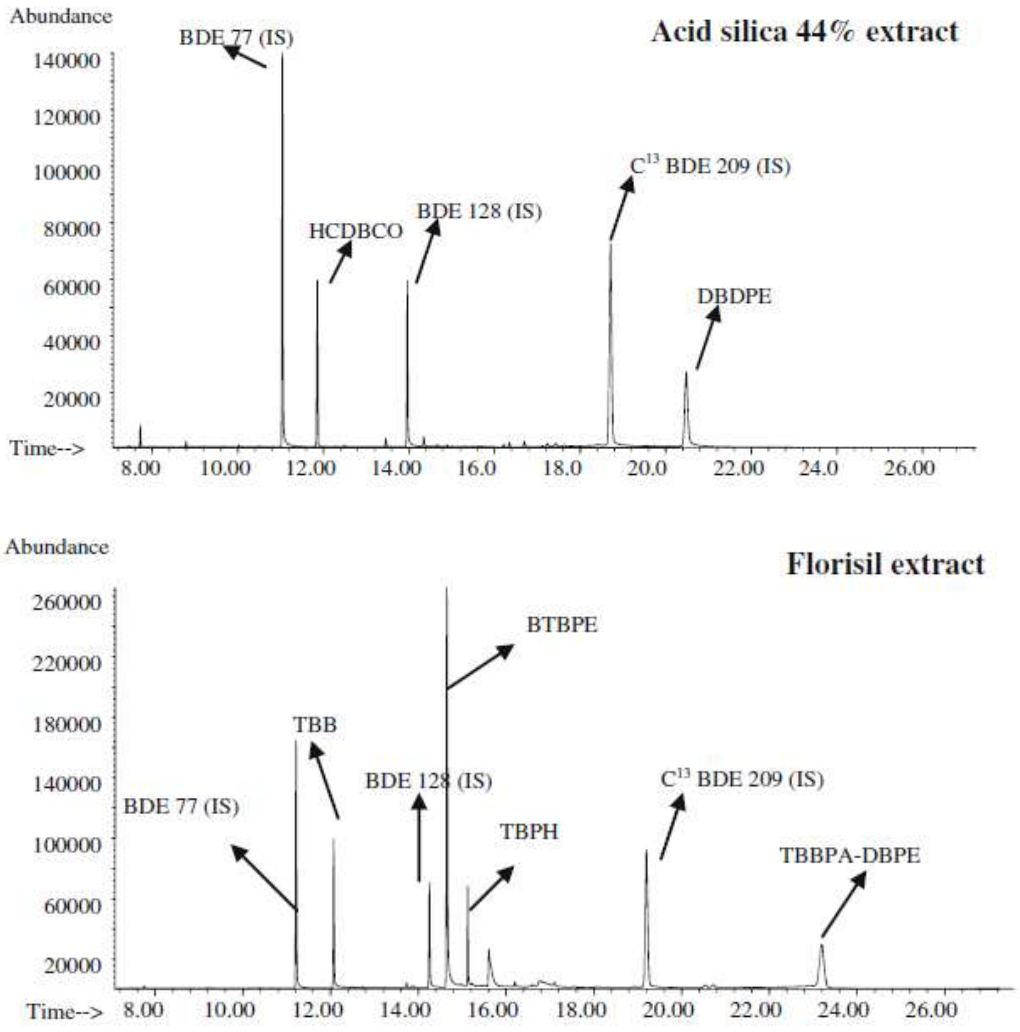
Kierkegaard et al, (2004) Environ. Sci. Technol.**, 38, 3247-3253**

DBDPE and BTBPE



Ali et al., (2011) Anal. Bioanal. Chem., **400, 3073-3083**

How to separate HCDBCO from TBB



Ali et al., (2011) Anal. Bioanal. Chem., **400, 3073-3083**

Concentrations observed in Dust

TABLE 2. Summary Statistics for DBDPE, BTBPE, HBCD, TBB, and TBPH Concentrations (ng/g) in Dust by Sample Type

	main living area				bedroom				home vacuum bag			
BFR	% detect	*n*	GM (GSD)	range	% detect	*n*	GM (GSD)	range	% detect	*n*	GM (GSD)	range
DBDPE	81%	16	138(5.4)	<10–11,070	86%	14	153(4.2)	<10–3,420	71%	7	39.4(6.7)	<10–262
BTBPE	100%	19	48.1(4.6)	4.7–654	100%	19	47.8(5.1)	1.6–789	100%	10	17.7(3.6)	2.5–219
HBCD	94%	16	354(8.6)	<4.5–130,200	93%	14	144(5.1)	<4.5–9,710	100%	7	282(11.6)	21.0–35,100
TBB	94%	16	322(5.9)	<6.6–15,030	86%	14	90.4(2.8)	<10.6–378	100%	7	91.1(2.6)	35.7–669
TBPH	100%	16	234(5.3)	3.0–10,630	100%	14	105(4.3)	1.5–763	100%	7	65.8(1.7)	24.3–111

PBT

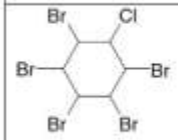
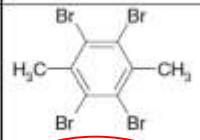
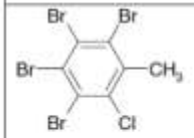
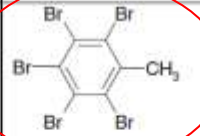
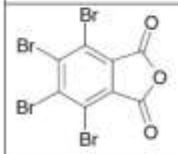
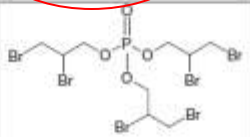
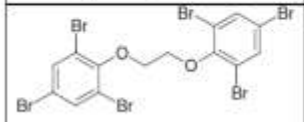
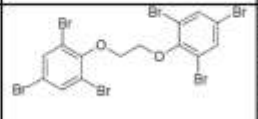
Anal Bioanal Chem (2011) 400:871–883
DOI 10.1007/s00216-011-4807-8

ORIGINAL PAPER

Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediments and suspended particulate matter

P. López · S. A. Brandsma · P. E. G. Leonards · J. de Boer

GC/ECNI-MS
m/z 79, 81

Molecular structure	Compound	Molecular structure	Compound
	Pentabromochlorocyclohexane PBCCH (isomers A, B, C and D) CAS [87-84-3] [a]MW = 513.09 [b]S_{water} =0.055 mg/L [c]Log $P_{octanol-water}$ = 4.72		2,3,4,5,6-Tetrabromo-*p*-xylene *p*TBX CAS [23488-38-2] MW = 421.75
	Tetrabromo-*o*-chlorotoluene TBoCT CAS[39569-21-6] MW = 422.19		2,3,4,5,6-Pentrabromotoluene PBT CAS [87-83-2] MW = 486.62 S_{water} =0.000935 mg/L Log $P_{octanol-water}$ = 6.99
	Tetrabromophthalic anhydride TBPhA CAS [632-79-1] MW = 463.7 S_{water} =0.016 mg/L Log $P_{octanol-water}$ = 5.63		Tris(2,3-dibromopropyl)phosphate TDBPP CAS [126-72-7] MW = 697.64 S_{water} =8 mg/L Log $P_{octanol-water}$ = 4.29
	1,2-bis(2,4,6-tribromphenoxy)ethane BTBPE CAS [37853-59-1] MW = 687.64 S_{water} =0.2 mg/L Log $P_{octanol-water}$ = 9.15		Decabromodipheylethane DBDPE CAS [84852-53-9] MW = 971.2 S_{water} =0.00072 mg/L Log $P_{octanol-water}$ = 11

Review about Novel BFRs

Environment International 37 (2011) 532–556

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journal homepage: www.elsevier.com/locate/envint

Review

Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour

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Thanks for listening