SOME LESSONS LEARNED TO PROTECT THE ANALYTICAL INSTRUMENT WHEN ANALYSING POPS IN PLASTIC
PART 2: STATIC EXTRACTION
PART 3: DISSOLVE AND PRECIPITATE

IPCP Webinar Series:
POPs in plastic and monitoring approaches
Part III: Extraction, clean-up, and analysis
of POPs in plastics
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The Fraunhofer IVV

Fraunhofer Institute for Process Engineering and Packaging IVV is one out of 72 institutes of the Fraunhofer Society.

Our work encompasses five business fields: Food, Packaging, Product Performance, Processing Machinery, and Recycling and Environment.

We have been running a POP analysis laboratory since the mid 1990ies:
PCDD/F, PBDD/F, BFR (PBDE, HBCD, …), PFAA, PFAS

Department Process Development Polymer Recycling works on plastic recovery processes for WEEE, ELV and B&C (e.g. ABS/PS from WEEE, PO from ELV, EPS from B&C)

Our test laboratories are accredited since 1996 and were re-accredited (D-PL-11140-04-00) in 2022 by the DAkkS (Deutsche Akkreditierungsstelle), the national accreditation body of the Federal Republic of Germany.

Process steps involved at Fraunhofer IVV
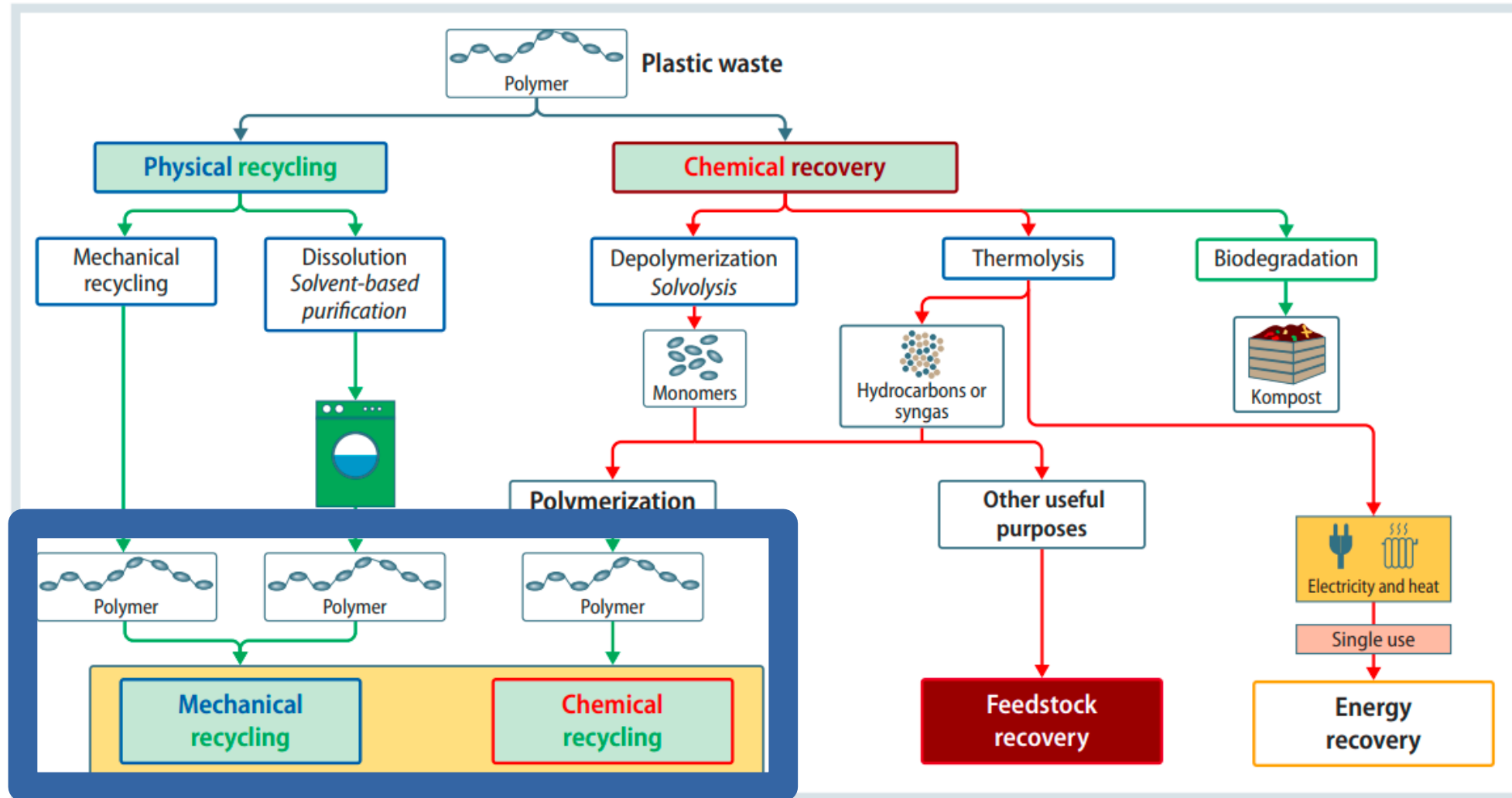
The Fraunhofer IVV – Past and Current European Projects

CloseWEEE

- Recycling of ABS, PC/ABS from WEEE
- CreaSolv® Process
- Re-application of recycled polymers in new EEE

Polystyreneloop

- Recycling of EPS from ETICs
- CreaSolv® removes HBCD for later destruction and Br recovery by pyrolysis
- Circular economy of EPS and bromine

NONTOX

- Recycling of polymers from WEEE, ELV, C&D
- POP analysis
- POP removal from plastics by CreaSolv®

Circular Flooring

- Soft-PVC from wasteflooring
- CreaSolv® removes pthalates
- Phtalates are destroyed and used as a raw material for new plasticizers

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Analytical instrumentation at Fraunhofer IVV - I

GC-Single quad-MS:
PBDEs, technical PCBs,
Phthalates, PAHs

LC-Triple quad-MS:
BPA, Nonylphenols, PFOS/PFOA

LC-GC:
MOSH/MOAH

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Analytical instrumentation at Fraunhofer IVV - II

GC-HRMS:
Dioxins, halogenated
Anisols, PBDEs

WD-XRF:
halogenated
plastics

+
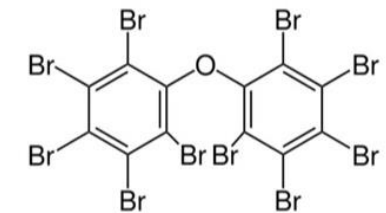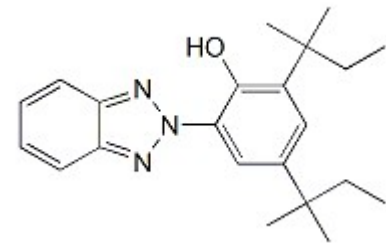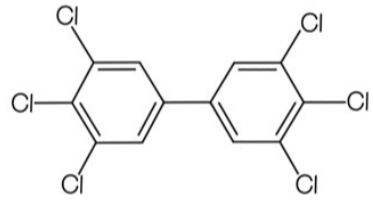
ICP-MS
ED-XRFA

LC-High resolution-QTOF
LC-High resolution-Orbitrap
GC-Orbitrap
GCxGC-single quad-MS
Headspace-GC-MS
GC-ECD
GC-EPED
etc.

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POPs analyzed at Fraunhofer IVV

|			
	Dioxins, PCP, Dioxin-like PCBs, halogenated phenols and anisols	Plasticizers like phthalates, DEHT, Adipates, DINCH and others	
	Plastics additives like UV and thermal stabilizers as well as their derivatives	PFAS and their precursors, volatile organic fluorine, bromine and chlorine	
	PBDEs and other brominated FRs like decabromodiphenyl ethane, HBCD and TBBPA	Phosphorous-based FRs like TBOEP, TCPP and TCEP	

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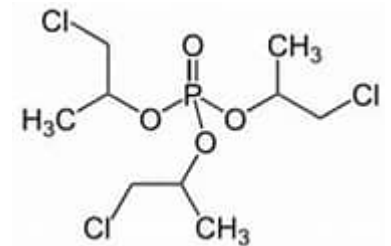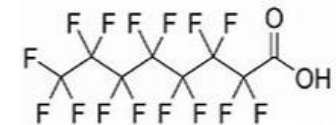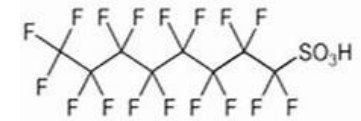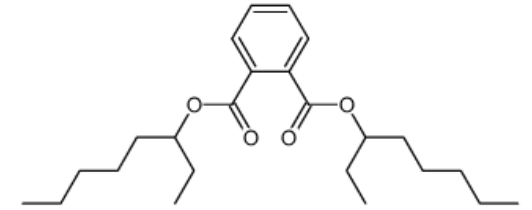
The mixed plastics matrix: A challenge

Reuse and recycling of end-of-life plastics remains very low at the moment, particularly in comparison with other materials such as paper, glass or metals. An EU Action Plan for a circular economy focusses on plastic materials, but there is the issue of safety and thus, the need for analyses.

Closed-loop recycling with a defined matrix is somewhat easy to handle. PET recycling is such a success story.

But performing analyses in differing matrices and/or mixed and unknown matrix is a challenge and needs a lot of experience and planning. Otherwise You can easily block Your laboratory.

We as an experienced POPs lab had to learn our lessons, too!

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The analytes: A further challenge

A recent study by UNEP has found that 13,000 chemicals are associated with plastics and plastic production across a wide range of applications, of which over 3,200 substances are of potential concern due to their hazardous properties.

Scientific knowledge and analytical capacity need to be strengthened to support effective decision making at the national and regional levels.

Performing analyses of such a wide range of chemicals in (already mentioned) variable matrix or mixed and unknown matrix is a huge challenge.
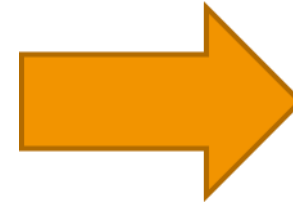
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Sources of plastic waste
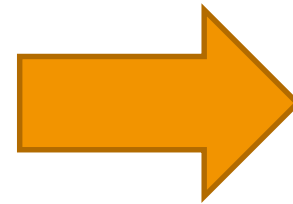
The material streams of interest are e.g.

- Closed loops for Food contact materials
- Textiles

and with less predictable composition

- Mixed house hold plastics
- WEEE and ELV
- Automobile scrap
- Building and construction waste

Individual methods possible

Complex planing and method adaption necessary

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Possible Analytical Problems

There is a number of possible problems when analyzing extracted plastic wastes:

- Some additives and impurities are present in very variable concentrations
- Oligomers and polymers are dissolved in your extracts and will destroy or at least contaminate the GC-column and the ion source of your MS
- Plasticizers are present in such amounts that they will issue solubility problems
- Monomers will polymerize during sample storage
- Samples are not clean, there might be dirt, debris and dust which disturb the analysis
- Some of the investigated compounds are ubiquitous (blanks!)
- Especially PBDEs might degrade during GC analysis

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Practical hints for extraction and analysis - 1

- Start with a proper planning. Try to collect as much information about your samples to be able to perform an appropriate sample prep and extraction as well as cleanup.

- Use XRF to collect further information on the samples. The bromine content will deliver information on the presence of brominated flame retardants. There are further indicator elements like chlorine etc.

- Perform tests with solvents for a better understanding of Your samples

- (if applicable) perform a washing with water if there is a lot of dirt and debris

- Keep extraction as simple as possible. Use XRF to test the extraction efficiency if possible, otherwise repetitive extraction might deliver validation data.

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Practical hints for extraction and analysis - 2

- Don't use milling and grinding as sample preparation unless it is unavoidable. Try to use cutting instead. Milled samples will lead to more amount of matrix present in your extract and thus, lead to analytical problems

- If milling is unavoidable cryo milling is recommended, but this will not solve the problem of representative sampling due to limited amounts (some grams)

Cutting and milling tools: preform cutter (left) and cryo mill (right)

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General rules for extraction and analysis - 3

- Use an appropriate clean-up step if necessary, e.g. addition of silica sulfuric acid for dirty samples or small silica columns for samples with high matrix content. Storage of the samples in the fridge may help either.

- Use proper high temperate columns for GC (e.g. the DB5-MS HT) and adequate column length (15 metre or shorter for PBDEs).
This is due to the fact that decabromo diphenyl ether (deca-BDE) can be easily degraded into nonabromo diphenyl ether and octabromo diphenyl ether when heated.
Therefore, chromatographic columns with shorter length are preferable.

- Start with the measurement of diluted samples (at least 1 : 10) and use splitless injection. Don't use split injection with undiluted samples.

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Why not to use split injection?

Let`s cite Wikipedia:

Most of vaporized sample goes to split vent

and let me object:

Your oligomers and polymers

will NOT VAPORIZE AT ALL

and

will stay at best in the liner!

Split/Splitless Injector   **Split Mode**

Restrictors

49 mL/min total **gas** flow

2 mL/min septum purge

46 mL/min to split vent

Split valve Open

Column flow always 1 mL

Most of vaporized sample goes to split vent

1 mL column flow

H e a t e d   H e a t e d

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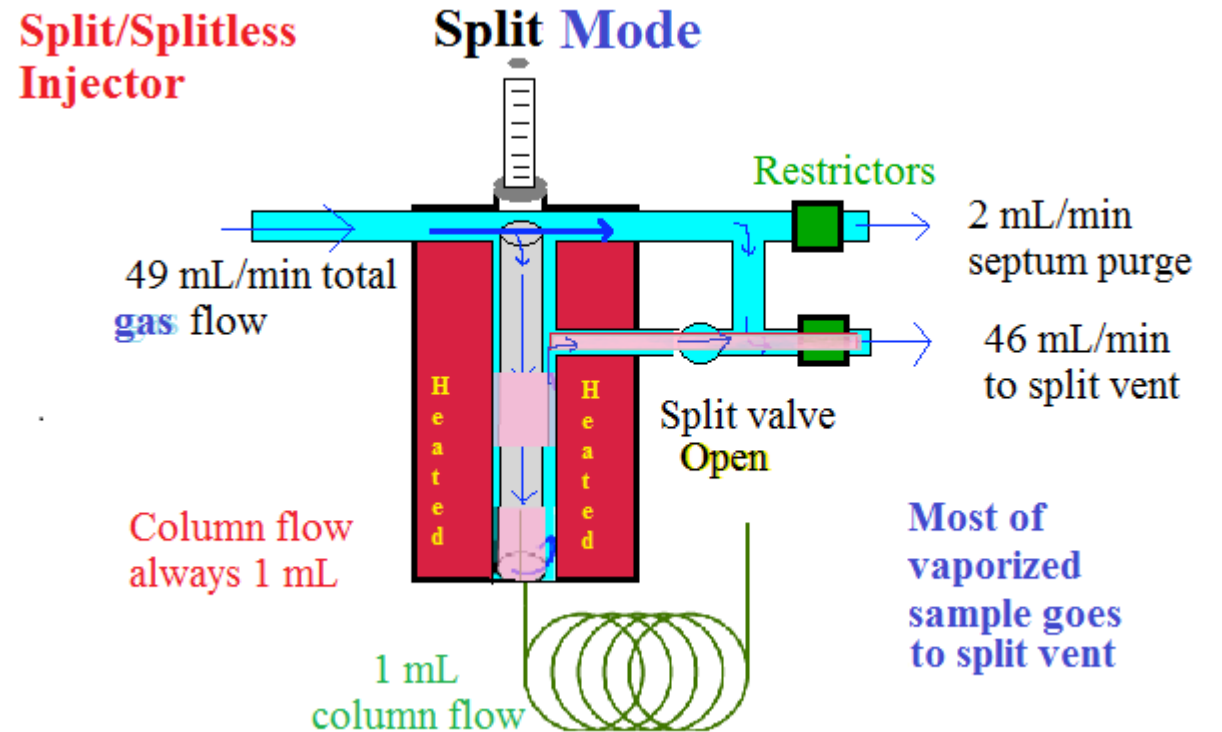
General rules for extraction and analysis - 4

- Test the temperature stability of your substances in the injector (variation of the injector temperature) and the needed temperature of the transfer line

- Perform tests with control standards regularly on Your GC-MS

- Always perform blank checks before and during the measurement campaign

Last but not least:

- Change Your liner after the measurement campaign and reduce the oven temperature when there are no measurements

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Why do You need an adequate solvent ?

Generally speaking, liquid extraction in chemistry is a separation process consisting of the <u>separation of substances from a solid matrix</u>.

If You can avoid it, do not dissolve the matrix with Your solvent. Otherwise You will need a precipation step.

It sounds obvious, but it is important to note:

- **It is not a good idea to inject dissolved matrix (=polymer) into a GC system. This might cause severe problems !**
- **Your analyte must be soluble in Your Solvent!**

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# Factors Influencing Solvent Extraction

- Time and Temperature

- Solubility of the analytes (up to 70% additive concentration in polymers) in sample and solvent

- Partition coefficient

- Diffusion coefficient in the polymer

- Swelling effects

- pH

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Diffusion coefficients in different polymers

Diffusion coefficients at 20° C, 40° C, and 60° C in different polymers (Brandsch et al, Polymers, 2021):

    (a) PP
    (b) GPPS
    (c) HIPS
    (d) ABS
    (e) SAN, and
    (f) PET

→Necessary extraction time may vary, grinding or milling is not necessary at all for polyolefines, GPPS is likely to be dissolved.

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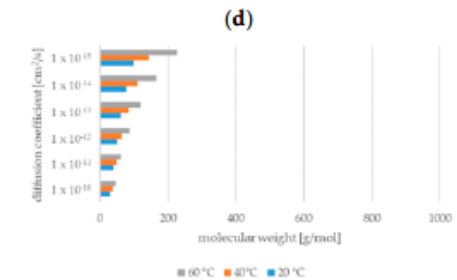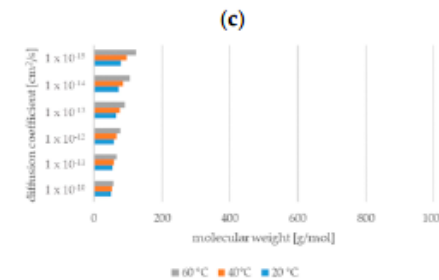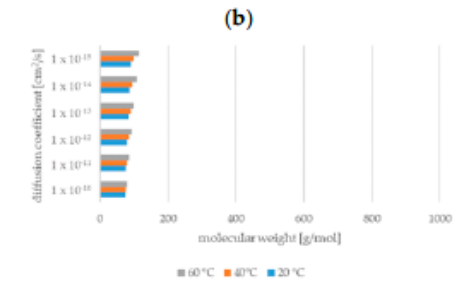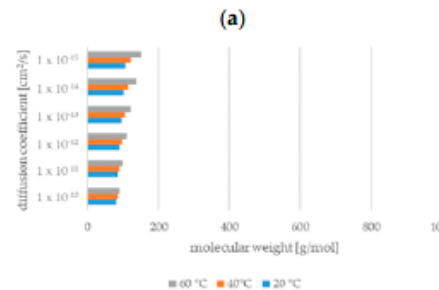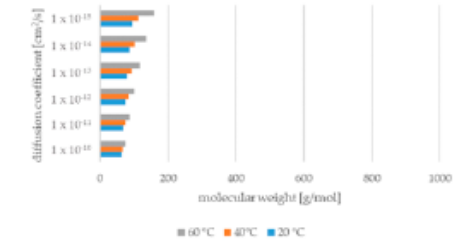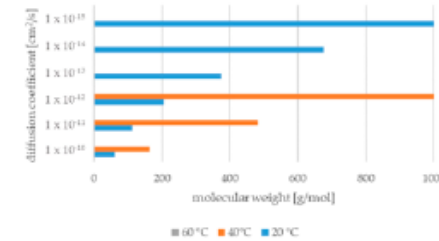
Where to get Diffusion Coefficients

Have a look on the website of Prof. Steven Abbott:

https://www.stevenabbott.co.uk/practical-solubility/diff-d-values.php

for details see T. Begley, L. Castle, A. Feigenbaum, R. Franz, K. Hinrichs, T. Lickly, P. Mercea, M. Milana, A. O'Brien, S. Rebre, R. Rijk & O. Piringer (2005): *Evaluation of migration models that might be used in support of regulations for food contact plastics*, Food Additives and Contaminants, 22:1, 73-90

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A short look on log K_{OW} of some POPs

- As with other persistent organic pollutants, due to their lipophilic behavior BFRs like PBDEs sorb to particulate organic matter within the environment. The log K_{OW} values (octanol-water partition coefficients) of the most commonly studied PBDEs range from 5.96 (BDE28) to 9.16 (BDE209), whereas Decabromo diphenyl ethane has a log K_{OW} of 3.55 and HBCD of 5.62.

- PFR (organophosphates) like tris(1-chloro-2-propyl) phosphate (TCPP) have a log K_{OW} of 2.59, triethyl-chloro-phosphate (TCEP) alog K_{OW} of 1.44 and tributyl phosphate (TBP) a log K_{OW} of 4.0. The low octanol-water partitioning coefficients of TCEP and TCPP resulted in becoming major contaminants detected in aquatic systems.

BTW, these values give us also a hint to choose the right extraction solvents.

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The PBDEs

Polybrominated diphenyl ethers or PBDEs, are a class of organobromine compounds that are used as flame retardants.
Due to the presence of bromine they have a relatively high weight and show a typical isotope pattern.

GC/MS characteristics of PBDEs (A) Chromatogram of bromide ions for selected PBDEs with the congener numbers listed.

Mass spectra for BDE- 47 under (B) EI and (C) ECNI (CH 4) ionization. The isotopic patterns for the dominant and second most abundant ions are shown next to their respective spectra according to Lin et al., 2015

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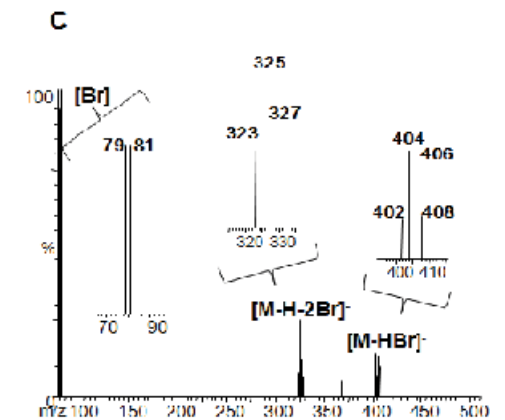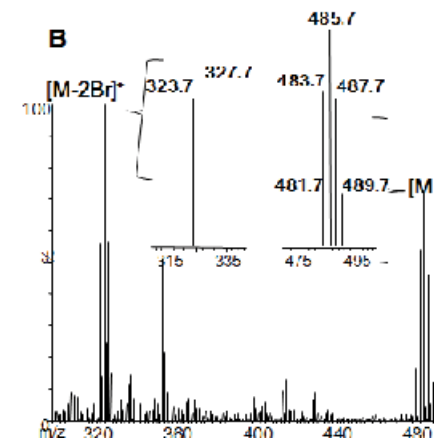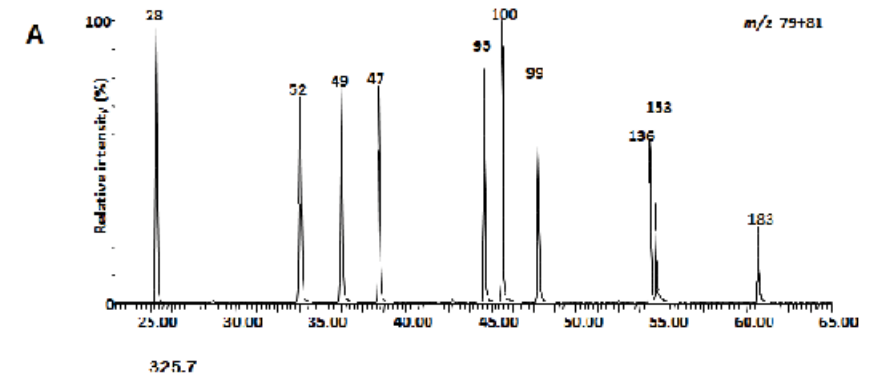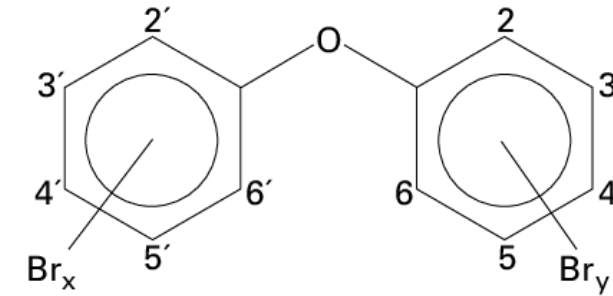
An easy and for most cases appropriate extraction approach: static extraction

Samples of polyolefines and textiles can extracted by static liquid extraction.

For this purpose, a quantity of approx. 0.5 g of the samples was weighed into a glass ampoule, 5 - 50 ml toluene are added and then extracted on a laboratory shaker at a constant temperature of 60 °C over a period of 24 hours.

1 ml of the supernatant is separated from the formed gel and subjected to GC analysis after passing a 0.45 µm PTFE syringe filter

A pretest with toluene is inevitable for mixed plastics!

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Example for analytical steps

Analysis of Reference materials (ERM-EC) consisting of polyolefine:

- ERM-EC590 (LDPE)
- ERM-EC591 (PP)

Static extraction can be performed without filtering.

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Example for analytical steps - analytes

List of determined PBDEs and PBBs

Analyte	CAS
2,4,4'-TriBDE (BDE-28)	41318-75-6
2,2',4,4'-TetraBDE (BDE-47)	5436-43-1
2,2',4,4',5-PentaBDE (BDE-99)	60348-60-9
2,2',4,4',6-PentaBDE (BDE-100)	189084-64-8
2,2',4,4',5,5'-HexaBDE (BDE-153)	68631-49-2
2,2',4,4',5,6'-HexaBDE (BDE-154)	207122-15-4
2,2',3,4,4',5,6'-HeptaBDE (BDE-183)	207122-16-5
2,2',3,3',4,4',6,6'-OctaBDE + 2,2',3,4,4',5,6,6'-OctaBDE (BDE-197 + 204)	117964-21-3 + 446255-54-5
DecaBDE (BDE-209)	1163-19-5
DecaBB (BB-209)	13654-09-6

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Example for analytical steps: GC-parameters

GC-Parameters:

- Injection temperature: 300 °C

- Injection method: splitless (1.2 min)

- Injection volume: 2 µl

- Carrier gas: Helium

- Column flow: 1.4 ml/min (constant flow)

- Oven temperature: 120 °C (2 min)

- 30 °C/min-230 °C (5.5 min)

- 20 °C/min-340 °C (3 min)

- Total program time: 19.67 min

- Column: Restek RTX-5 (15 m x 0.25 mm, 0.1 µm)

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Example for analytical steps: MS-parameters 1

The instrument, a low-resolution GC-MS instrument (Shimadzu QP2010 Plus), operated in Single Ion Monitoring mode (SIM), monitoring two fragment ions per analyte. PBDEs and PBBs in the prepared sample extracts were quantified via the internal standard substances.

- <u>MS-Parameters:</u>

- Ione Source Temperature: 230 °C

- Interface Temperature: 300 °C

- Ionization Mode: EI+

- Solvent cut time: 3.5 min

- Mass fragments and retention time: see following table

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Example for analytical steps – parameters 2

Mass fragment table of native analytes and internal standards with retention time

Analyte	Retention Time [min]	Calibration Mass [m/z]	Reference Ion [m/z]
BDE-28 / BDE-28L	5.53 / 5.52	248 / 260	406 / 418
BDE-47 / BDE-47L	6.39 / 6.38	326 / 338	486 / 498
BDE-99 / BDE-99L	7.88 / 7.87	404 / 416	563 / 575
BDE-100 / BDE-100L	7.46 / 7.45	404 / 416	563 / 575
BDE-153 / BDE-153L	10.57 / 10.56	643 / 655	484 / 496
BDE-154 / BDE-154L	9.48 / 9.47	643 / 655	484 / 496
BDE-183 / BDE-183L	13.12 / 13.11	721 / 733	561 / 573
BDE-197 + 204 / BDE-197L	14.61 + 14.49 / 14.60	641 / 653	801 / 813
BDE-209 / BDE-209L	16.94 / 16.93	799 / 811	400 / 407
BB-209 / BB-209L	16.28 / 16.27	783 / 795	623 / 635

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Data evaluation with Xcalibur Qual and Quan

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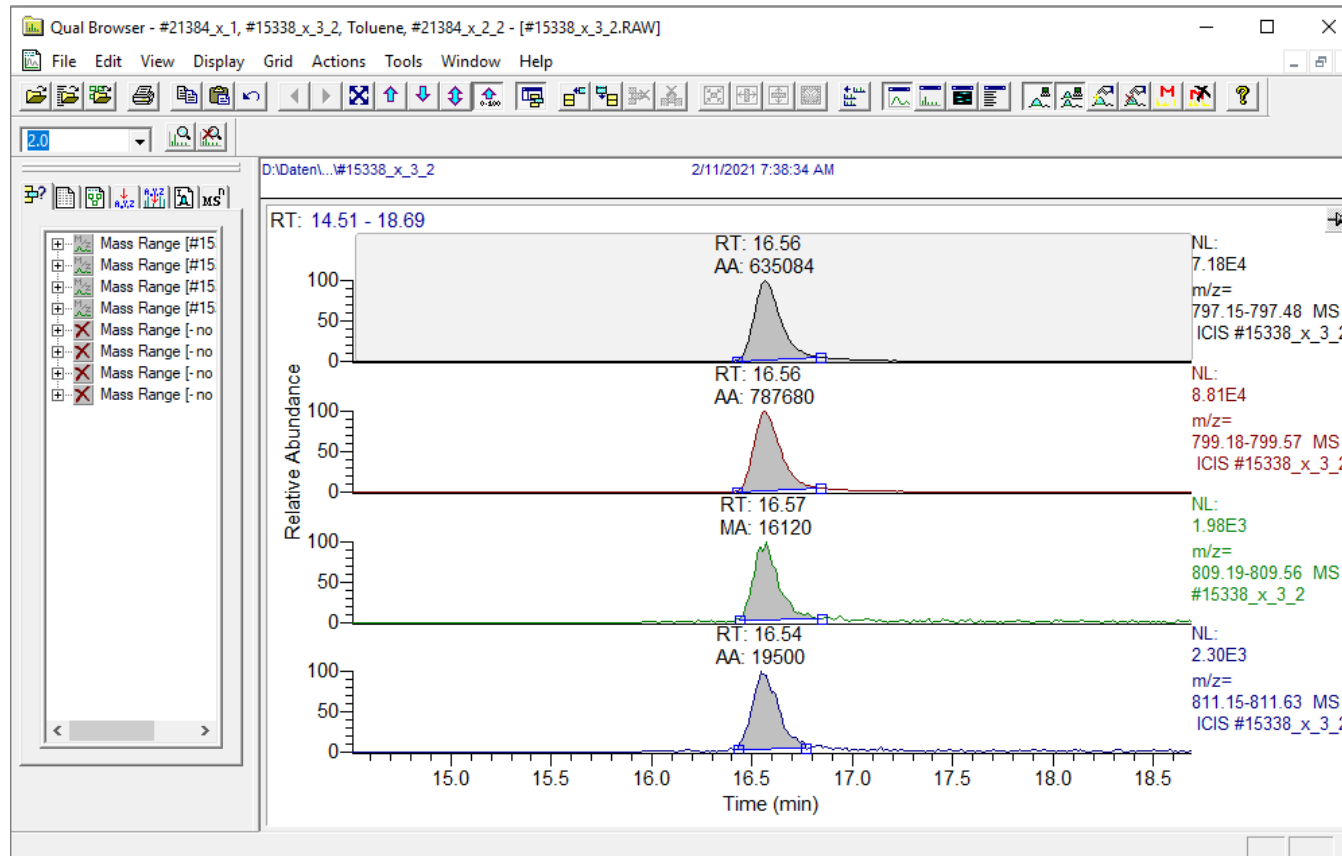
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Example for analytical steps – results

RM code/item ERM-EC590			Analyte BB-209	Description POLYETHYLENE (LDPE)		
Sample number	Internal sample code	Customer's bottle number	Number single experiment	Concentration in the material [mg/kg] [1]	Average per sample [mg/kg]	SD per sample
1	#23721	01501	replicate 1	668.53	674.83	12.01
			replicate 2	688.68		
			replicate 3	667.27		
2	#23722	01502	replicate 1	641.34	651.42	10.01
			replicate 2	651.57		
			replicate 3	661.36		
3	#23723	02185	replicate 1	625.61	619.66	7.71
			replicate 2	622.42		
			replicate 3	610.95		
4	#23724	02335	replicate 1	579.28	582.87	4.01
			replicate 2	587.19		
			replicate 3	582.14		
Average all samples [mg/kg] LOD				632.19 12.5		
SD all samples				36.89		
Certified value [mg/kg]				630		
Deviation from the certified value [%]				0.3		
Uncertainty U_{rel} [%] [2]				11.7		

1) The values refer to the content of the analytes in microgram per kilogram of the sample.
   LOD: Limit of Detection

2) The uncertainty is the expanded uncertainty estimated in accordance with DIN ISO 11352, with a coverage factor k = 2, corresponding to a level of confidence of about 95 %.

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Example – Static extraction validation

- The Validation of the extraction process of the samples was validated with X-Ray fluorescence analysis (XRF). A Spectro XEPOS XRF spectrometer was used as the measuring device. The measurements were carried out using the standard method for plastics.

- The customer samples were analyzed before and after extraction using XRF to determine the bromine content and, in addition, the antimony content. This enabled the extraction yield of bromine and antimony to be determined.

- For the measurement using energy-dispersive XRF (ED-XRF), approx. 0.5 g each of the original samples and the extracted samples were weighed into plastic cuvettes, which were fitted with a 4 µm Prolene® film.

- The extraction yield of bromine was over 99% for both sample materials. Thus, the 1st static extraction was used for the analysis. Further clean-up turned out to be not necessary.

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Dissolve and precipitate – v1

An approach is to dissolve the plastic sample completely in tetrahydrofurane, precipitate any polymer with hexane or ethanol, filter (and if necessary then dilute the solution with cyclohexane) and analyse it on the GC-MS

- Example PS foams:
  Samples were dissolved in tetrahydrofurane (10 wt%) and precipitated by addition of the fivefold amount EtOH.
  Wait for 1day, then
  1 ml of the supernatant is separated from the formed gel
  and subjected to GC analysis after passing a 0.45 μm
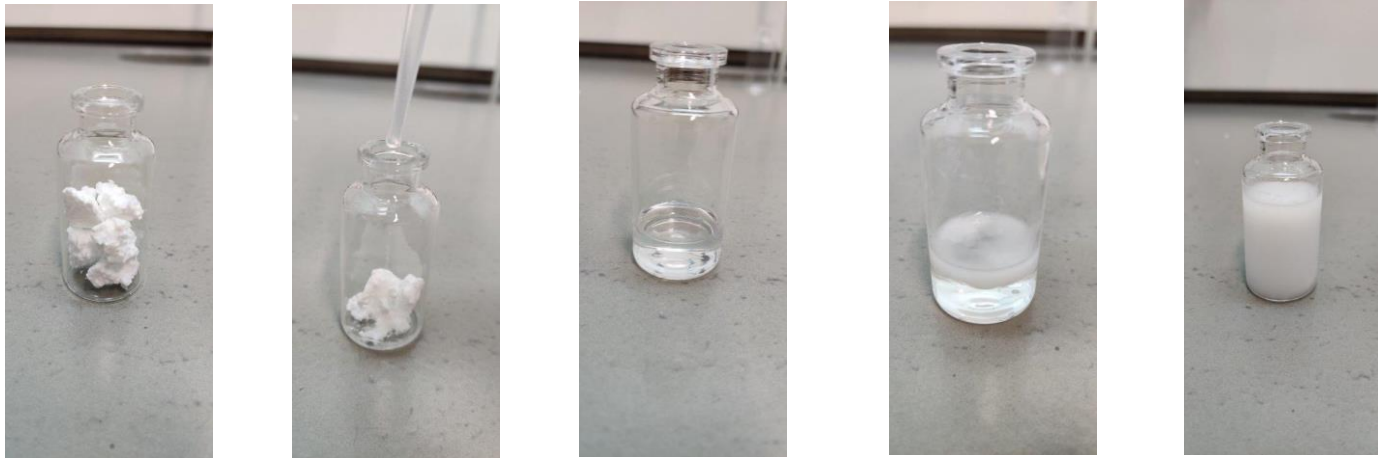 PTFE syringe filter.

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Dissolve and precipitate - v1

- As an additional step LLE in hexane under addition of water is possible

Example:

- Dissolve and precipitate steps

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Dissolve and precipitate – v2

If You have started with static extraction and toluene dissolves Your matrix, use 1 ml of Your toluene extract and add 5 mL of hexane to precipitate.

After some hours filter an aliquot of 1 mL (and if necessary then dilute the solution with cyclohexane)

and analyse it on the GC-MS …..

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Additional steps

- Column cleanup

- Sulforic acid silica

- SEC

- Addition of silica

- ….

But: take care for blanks and stability!

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Thank you for your attention !

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