

# IPCP Webinar Series: POPs in plastic and monitoring approaches

Part III: Sampling of plastics from major sectors to monitor POPs in plastics; 23.5.2023



## Introduction to the Stockholm Convention “Draft guidance on sampling, screening and analysis of persistent organic pollutants in products and recycling” PART 2

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# Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

The monitoring guidance has a step by step approach to monitor POPs in products and recycling and these steps are elaborated for the major POPs groups.

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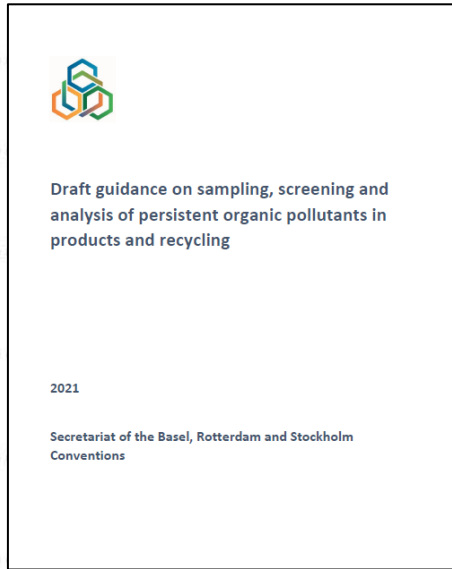
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# Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

## Step 4: Quantification of POPs in products and recycling.

- The guidance include for main matrices technical information on extraction and clean-up of samples and information of sample preparation.

4.5	Sample preparation, extraction and clean-up.....
4.5.1	Preparation of polymer/plastic samples .....
4.5.2	Extraction of POP-BFRs from polymers.....
4.5.3	Extraction of PBDEs in flexible and rigid polyurethane foam.....
4.5.4	Extraction of HBCD from textiles.....
4.5.5	Specific considerations on quality assurance .....



- Sample preparation need to be adjusted & optimized to the complex materials like plastic.
- Care has to be taken that the polymers do not contaminated the instruments (MS) and GC-columns. Optimized clean-up!!!

# Step by step approach for monitoring PBDE in articles and products

## Step 4: Quantification of POPs in products and recycling

- For the individual POPs the guidance contain sections on quantitative (and sometimes semiquantitative) methods.

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# Guidance on monitoring of POPs in products and recycling – Referencing to available international standards

## Step 4: Quantification of POPs in products and recycling

### The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of the respective POPs in products (also mention limitations for products)

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6.7.5	Determination of SCCPs in water (ISO 12010:2019) .....	



# Guidance on monitoring of POPs in products and recycling – Referencing to available international standards

## Step 4: Quantification of POPs in products and recycling

- For a number of product matrices no international standards are available for sampling, extraction & clean-up.
- For those, where available, some inhouse methodologies used by laboratories experienced in the analysis of POPs in products and recycling are described.
- The guidance further describe case studies (Annex 2) with reference to some reports where monitoring or analytical procedures for a POP in certain product matrix is described.



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# Examples for instrumental setting for individual POPs

Annex 3 contain for each of the POPs a full analytical method for instrumental analysis

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# Examples for instrumental setting for individual POPs

- One example of a full instrumental setting is given for each of relevant POP in products/plastic.
- Example here for PBDE analysis
- With a suggested temperature program
- And options of GC columns including column length
- The method options are from experienced commercial or national laboratories.

**Table A3-A1:** GC/MS conditions for PBDE

Instrument	LRMS or HRMS
Column	DB-5MS or ENV-5MS 15 m × 0.25 mm I.D. (0.1 μm) (5% Phenyl Polysilphenylene-siloxane)
GC program	120 °C (1 min) – 20 °C/min – 200 °C – 10 °C/min – 300 °C (10 min)
Inj.	On Column
Guard col.	Deactivated capillary 0.5 m × 0.53 mm I.D.
Inj. Temp.	120 °C (0.1 min) – 100 °C /min – 300 °C (15 min)
Inj. Volume	2 μL
Carrier gas	He (1.0 mL/min)
Ionization	El
Electron Voltage	30~40 eV
Trap Current	500 μA
Accelerated Voltage	8 kV
Interface temp.	300 °C
Ion source temp.	300 °C
Detection	SRM (e.g., SIM)
Resolution	High resolution or low resolution



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# Examples for instrumental setting for individual POPs

- Full masses for the individual POPs are provided for high resolution mass spectroscopy setting which can be used with reduced digits also for low resolution mass spectrometry.
- For chlorinated and brominated POPs having isomer clusters two masses for each homologue are given (for quantification and confirmation)
- This includes also the masses of the respective  $^{13}\text{C}$  standards

Table A3-A2: Masses of detected ions ( $m/z$ 's) for PBDE (HRMS masses; for LRMS reduced)

Compounds within GC time windows	Quantification	Confirmation
Tetrabromodiphenylether	485.7112	483.7132
Pentabromodiphenylether	563.6216	565.6197
Tetrabromo[ $^{13}\text{C}_{12}$ ]diphenylether	497.7513	495.7534
Perfluorokerosene	492.9697	
Pentabromodiphenylether	565.6197	563.6216
Hexabromodiphenylether (M-2Br)	483.6955	481.6975
Heptabromodiphenylether (M-2Br)	561.6060	563.6040
Pentabromo[ $^{13}\text{C}_{12}$ ]diphenylether	577.6598	575.6618
Hexabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	495.7357	493.7377
Heptabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	573.6462	575.6442
Perfluorokerosene	530.9664	
Hexabromodiphenylether (M-2Br)	483.6955	481.6975
Heptabromodiphenylether (M-2Br)	561.6060	563.6040
Heptabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	573.6462	575.6442
Perfluorokerosene	566.9665	
Octabromodiphenylether (M-2Br)	641.5145	639.5165
Octabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	653.5546	651.5567
Perfluorokerosene	642.9601	
Nonabromodiphenylether (M-2Br)	719.4250	721.4230
Nonabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	731.4651	733.4631
Perfluorokerosene	730.9537	
Decabromodiphenylether (M-2Br)	799.3335	797.3355
Decabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	811.3737	809.3757
Perfluorokerosene	804.9505	



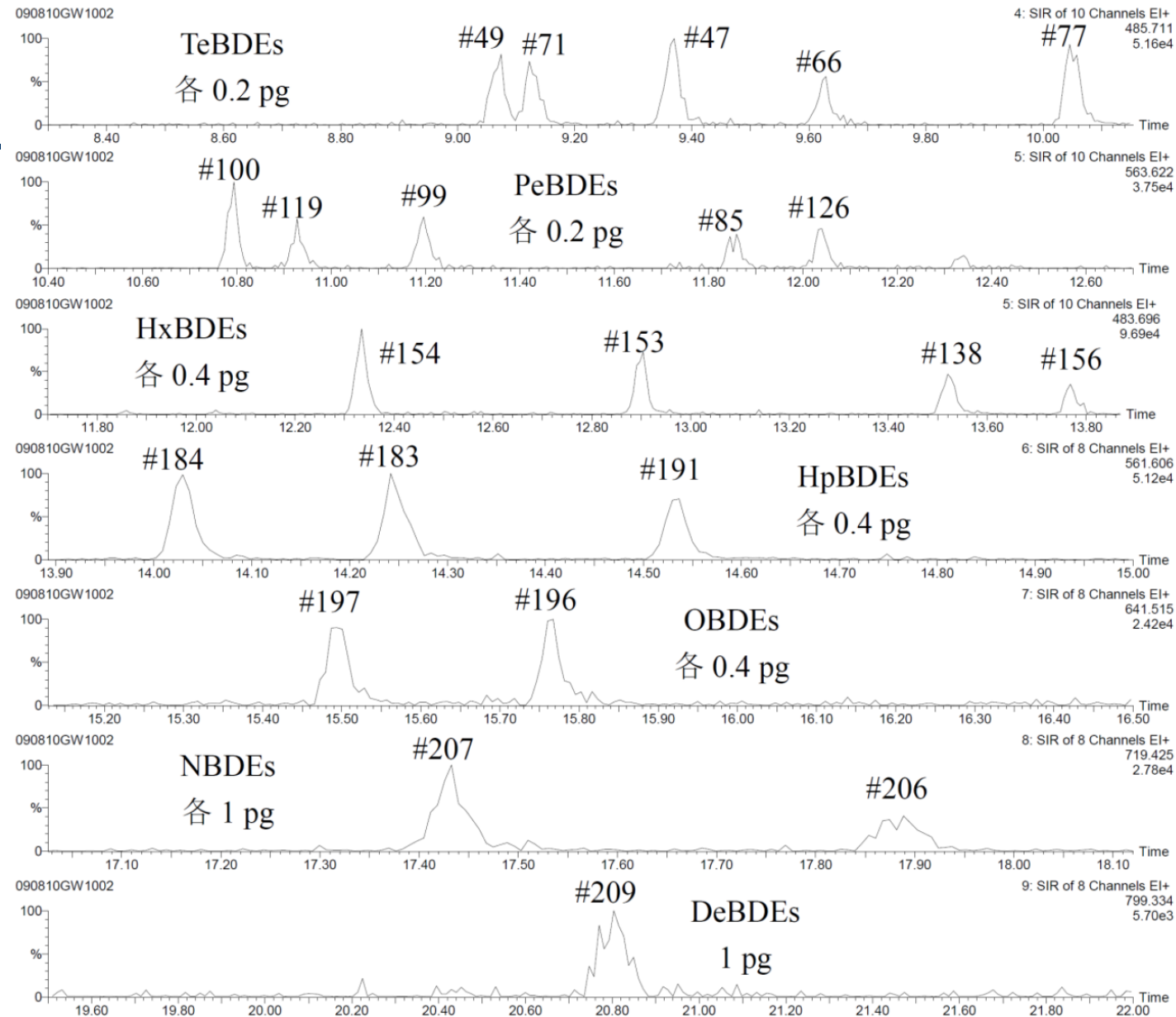
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# GC Chromatograms for individual POPs

- GC Chromatograms are provided for the individual POPs: Example PBDEs
- With assignment of individual congeners.



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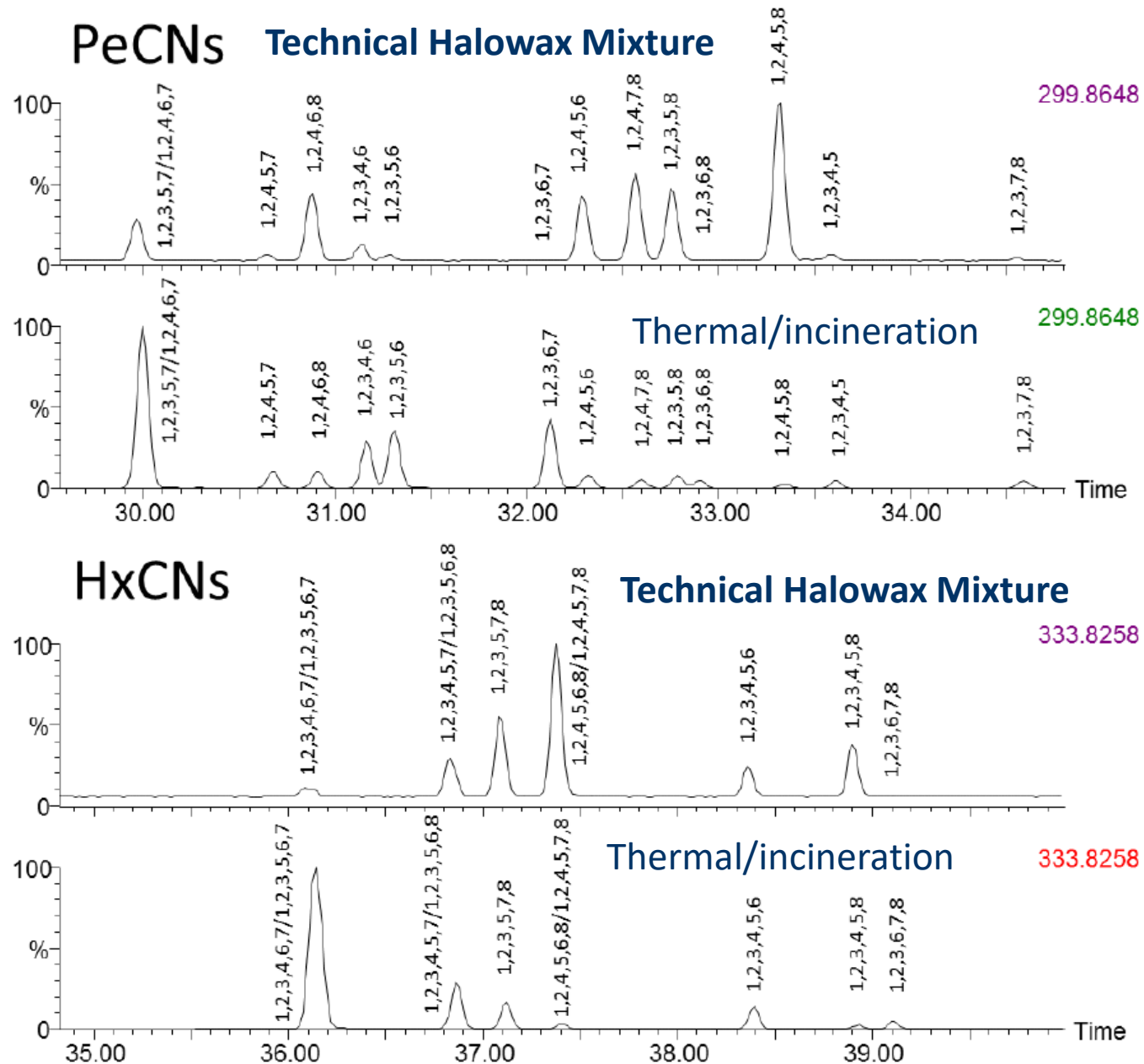
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# GC Chromatograms for individual POPs

## GC Chromatograms are provided for the individual POPs: Example PCNs

- For PCNs the chromatograms of technical PCN mixtures are provided which might be found in plastic cables (1930 to 1970) or neoprene rubber (until 2000) and related recycling.
- Also the thermal pattern of unintentional PCN from incineration samples including open burning or fires is provided for comparison.



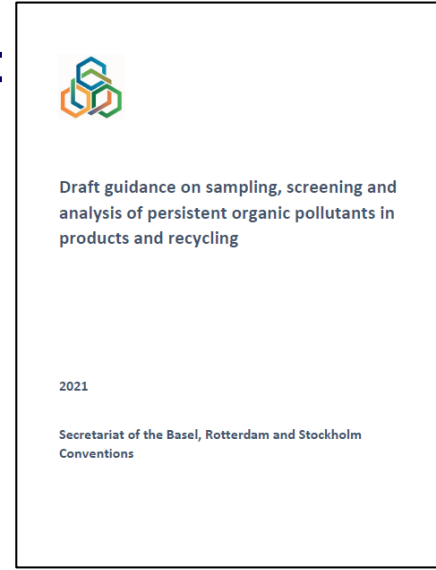
# Examples for instrumental setting for individual POPs

Annex 3 contain for each of the POPs a full analytical method for instrumental analysis

**ANNEX 3**      **Examples for instrumental analysis ..... 153**

For chlorinated paraffins three analytical methods are described in the guidance:

- A low resolution GC/ECNI-LRMS (electron-capture negative ionization) method which would also be suitable for developing countries
- A high resolution GC/HRMS method with „Orbitrap“
- The LC-MS/MS method of the National Institute for Environmental Studies (Tsukuba, Japan) which allows the monitoring of SCCP, MCCP and LCCP.



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# Examples for instrumental setting for individual POPs

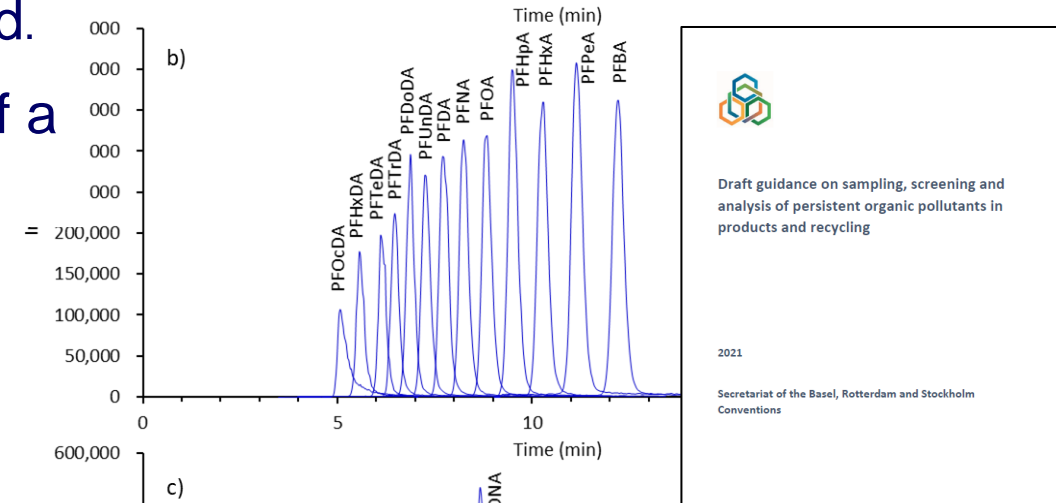
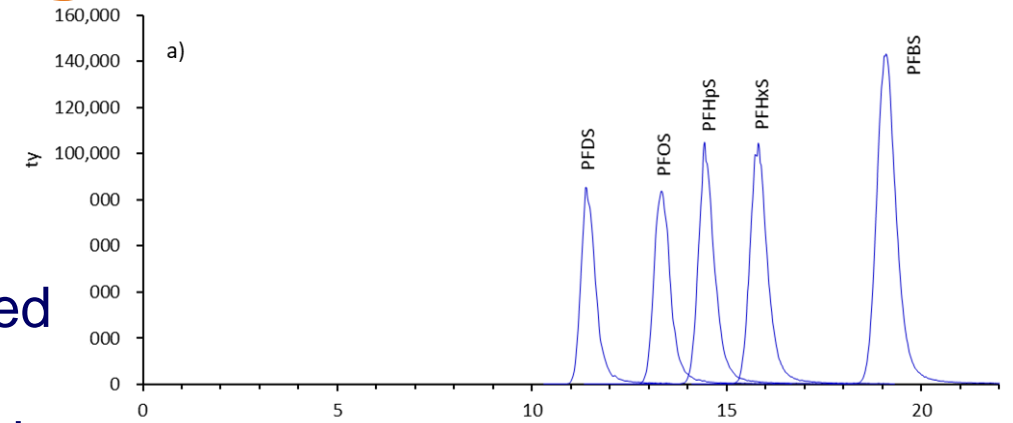
Annex 3 contain for each of the POPs a full analytical method for instrumental analysis

**For POP PFAS three analytical methods are described:**

- Two LC-MS methods are described. One method provided by National Institute of Advanced Industrial Science and Technology (AIST) is according to ISO 21675 method.
- A GC/MS method which has been developed in a PhD of a Kenyan researcher (Professor Francis Orata).
- One challenge is that for most of PFOA/PFAS related substances (several 100!) no analytical standard is available for the quantification of e.g. PFOA related compounds.
- Currently the TOP-Assay is the most comprehensive approach for quantification of the complex precursor

Annex 3-I-1: LC-MS/MS analysis of PFOS, PFOA, PFHxS (inst

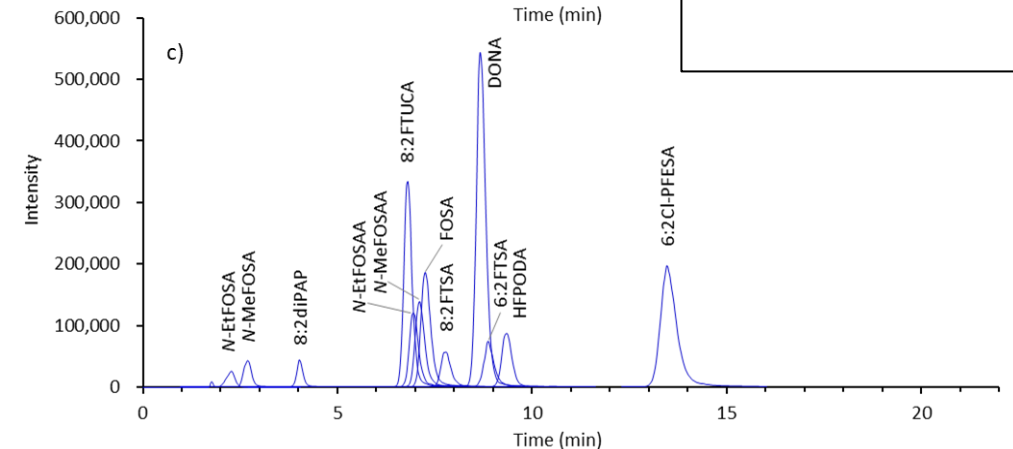
Annex 3-I-2: GC-MS/MS analysis of PFOS, PFOA and PFHxS



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# Need of further update of the guidance for monitoring POPs in products and recycling

The guidance on POPs in products and recycling is updated when needed:

What information to be added in the next update?

- Inclusion of monitoring methods for the new listed POPs 2023: UV-328 and Dechlorane Plus
- Inclusion of useful case studies published 2022/2023
- New international (and national standards) on analysis of POPs in products and recycling (e.g. ISO is developing monitoring standards for textiles)



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# Thank you for your attention !



## More Information

UNEP Chemical in Plastics: [www.unep.org/resources/report/chemicals-plastics-technical-report](http://www.unep.org/resources/report/chemicals-plastics-technical-report)

UNEP Plastics Treaty: <https://www.unep.org/about-un-environment/inc-plastic-pollution>

Basel Convention: [www.basel.int](http://www.basel.int)

Stockholm Convention: <http://chm.pops.int/>

Rotterdam Convention: [www.pic.int](http://www.pic.int)

SAICM: <http://www.saicm.org/>

IOMC/OECD: <https://iomctoolbox.org/>; <http://www.oecd.org/chemicalsafety/>

Science: [www.ipcp.ch](http://www.ipcp.ch); [www.foodpackagingforum.org/](http://www.foodpackagingforum.org/); [www.isde.org/](http://www.isde.org/); <https://ikhapp.org/scientistscoalition/>

Industry: <https://endplasticwaste.org/>; <https://plasticseurope.org/>; <http://www.suschem.org/>

NGO: [www.ipen.org](http://www.ipen.org); [www.ciel.org/](http://www.ciel.org/); [www.ban.org](http://www.ban.org); [www.chemsec.org](http://www.chemsec.org); [www.wecf.org](http://www.wecf.org); <https://chemtrust.org/>

**Better-world-links:** <http://www.betterworldlinks.org/>; <https://www.plasticstreaty.org/scientists-declaration/>

