

Draft guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles

Relevant to the substances listed in Annexes A, B and C
to the Stockholm Convention on Persistent Organic Pollutants
in 2009 and 2011

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DRAFT

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List of abbreviations and acronyms

ABS	Acrylonitrile-butadiene-styrene
ACN	Acetonitrile
ASR	Accelerated solvent extraction
BFR	Brominated Flame Retardant
CEN	European Committee for Standardization
CME	Cellulose mixed ester
c-OctaBDE	Commercial Octabromodiphenyl ether
c-PentaBDE	Commercial Pentabromodiphenyl ether
COP	Conference Of Parties
CRT	Cathode Ray Tube
DART	Direct Analysis in Real Time
DecaBDE	Decabromodiphenyl ether
ECD	Electron Capture Detector
EEE	Electrical and Electronic Equipment
EI-MS	Electron Impact Mass Spectrometry
EPED	Echelle-Plasma-Emission-Detector
FPF	Flexible Polyurethane Foam
FR	Flame Retardant
GLP	Good Laboratory Practice
HBB	Hexabromobiphenyl
HBCDD	Hexabromocyclododecane
HIPS	High Impact Polystyrene
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
LC	Liquid chromatography
LIBS	Laser-Induced Breakdown Spectrometry
LOD	Limit of detection
LRMS	Low resolution mass spectrometry
LCqMS	Liquid chromatography quadrupole mass spectrometry
MAE	Microwave-Assisted Extraction
MeOH	Methanol
MTBE	Methyl tert-butyl ether
NIR	Near Infrared
PAPs	Polyfluorinated Alkyl Phosphate Esters
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PBDD/PBDF	Polybrominated Dibenzo-p-dioxins and Polybrominated Dibenzofurans
PBDE	Polybrominated Diphenyl Ether

PBT	Polybutylene Terephthalate
PC	Polycarbonate
PCB	Polychlorinated Biphenyl
PCDD/PCDF	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PET	Polyethylene Terephthalate
PeCB	Pentachlorobenzene
PFAS	Per- and Polyfluorinated Alkylated Substance
PFCs	Per- and Polyfluorinated Chemicals/Compounds
PFDA	Perfluorodecanoic acid; Perfluorodecanoate
PFDoA	Perfluorododecanoic acid; Perfluorododecanoate
PFHpA	Perfluoroheptanoic acid; Perfluoroheptanoate
PFHxA	Perfluorohexanoic acid; Perfluorohexanoate
PFNA	Perfluorononanoic acid; Perfluorononanoate
PFOA	Perfluorooctanoic acid; Perfluorooctanoate
PFOS	Perfluorooctane Sulfonic Acid; Perfluorooctane Sulfonate
PFOSF	Perfluorooctane Sulfonyl Fluoride
PLE	Pressurised Liquid Extraction
POPs	Persistent Organic Pollutants
POP-PBDEs	Persistent Organic Pollutant polybrominated diphenyl ethers (the PBDEs listed in the Convention)
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PXDD/PXDF	Polybrominated-chlorinated dibenzo-p-dioxins and dibenzofurans
QA/QC	Quality assurance and quality control
RoHS	Restriction of the use of certain hazardous substances in electrical and electronic equipment
SCCP	Short Chain Chlorinated Paraffin
SC	Stockholm Convention
SIM	Selected ion monitoring
SPE	Solid phase extraction
TBBPA	Tetrabromobisphenol A
THF	Tetrahydrofuran
TOF	Time of Flight
UAE	Ultrasonic-assisted extraction
WD-XRF	Wavelength dispersive XRF
WEEE	Waste Electrical and Electronic Equipment
XRF	X-Ray Fluorescence
XRT	X-Ray Transmission

1 Introduction

1.1 Stockholm Convention background on POPs listed in 2009 and 2011

In 2009 and 2011 ten new substances were listed in the annexes to the Stockholm Convention. Several of these newly listed POPs have been used or are still used in various products and articles (see Annex 1-A).

A set of guidance has been developed to assist parties to meet their obligations relevant to the POPs listed in 2009 and 2011, such as the guidance for developing inventories (Stockholm Convention 2012a¹, b²) and for applying best available technologies and best environment practices (Stockholm Convention 2012c³, d⁴) giving also an insight on former uses of these substances and their relevance for the current presence of POPs in articles. The draft guidance is available in document UNEP/POPS/COP.6/INF/15. Among the new listed POPs in the Stockholm Convention, pentachlorobenzene (PeCBz) was listed in Annex C can be present as unintentional by-product in a range of products and articles (see Annex 1-C).

While production of POP-PBDEs is considered to have stopped in 2004 and therefore these substances are now contained only in articles in use and in the recycling flows, PFOS is still produced in at least three countries (China, Germany and Italy) and possibly also used in a range of new articles and processes where exemptions and acceptable purposes have been granted by the Convention (see Annex 1-A). Furthermore, PFOS might be still used by parties having not ratified the amendments of the Stockholm Convention or by non parties.

POP-PBDEs and PFOS are also included in larger re-use and recycling flows (e.g. used electrical and electronic equipment EEE, waste electrical and electronic equipment WEEE plastics for recycling, second hand vehicles, synthetic carpets, certain furniture, textiles, and paper). POP-PBDEs are included with a time-limited exemption allowing for the recycling of wastes containing these substances and their subsequent use in articles until 2030. Therefore, the guidance for recycling and disposal of POP-PBDE has been developed (Stockholm Convention 2012c)⁴. This guidance considers the recommendations adopted by decision SC-5/5 of the Conference of the Parties to the Stockholm Convention on separation of POP-PBDEs containing materials from the recycling streams, as outlined in annex to decision POPRC-6/2. This requires to a reasonable extent monitoring of these recycling streams, including the products made from the recycled materials, for POP-PBDE content, to ensure their environmentally sound management (Stockholm Convention 2012c)⁴. In case of PFOS and related substances, recycling of articles is not allowed and therefore products at the end of their life have to be managed in an environmentally sound manner. Also this may require monitoring of material flows potentially contaminated with PFOS and related substances.

Furthermore, for developing inventories of the newly listed POPs, monitoring of POPs content in articles would be also useful.

¹ Stockholm Convention (2012a) Guidance for the inventory of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs (Draft).

² Stockholm Convention (2012b) Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs (Draft).

³ Stockholm Convention (2012c) Guidelines for recycling and disposal of POP-PBDE containing articles (Draft).

⁴ Stockholm Convention (2012d) Guidelines on best available techniques and best environmental practices for the production and use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs (Draft).

1.2 Purpose and objective of this guidance

This document provides guidance on monitoring (sampling, screening and analysis) of the POPs content in articles and products in use and in the recycling streams for those POPs listed in 2009 and 2011.

Guidance is provided:

- On articles and products possibly containing the POPs listed in 2009 and 2011;
- To develop strategies for monitoring of POPs in articles/products and recycling streams;
- On inventory development aspects such as determining emission/impact factors;
- For import control and possible monitoring at customs or at consumer protection level;
- For the assessment of human exposure through articles in use and through recycled materials.

Please Note: This guidance does not aim to develop analytical standard procedures similar to e.g. ISO or CEN standards. This document rather gives support and advice for monitoring some POPs listed in 2009 and 2011 with practical information on sampling, screening, and basics on extraction and analysis of samples. Where available the guidance refers to international standards developed for analysis for these chemicals.

1.3 Types of articles and products

Major articles, products and other material, which may contain POPs⁵ listed in 2009 and 2011, are described in Annex 1. Where available, case studies on monitoring campaigns are referenced and/or provided in Annex 3.

1.4 Approach to combine screening with confirmation analysis

The guidance gives an introduction to screening approaches. This includes screening technologies for bromine or fluorine. In addition, droplet test for repellency, or combustion chromatography for element screening are described. Such screening enables relatively cheap and simple pre-selection of some article groups with regards to their possible POPs content (e.g. PUR foams for bromine as indication of POP-PBDE content, or carpets for fluorine as indication for PFOS). It helps to minimise the time and expenses for confirmation analysis, which requires extraction and appropriate clean-up steps. For final confirmation or quantification by instrumental analysis basic information is provided, including examples of instrumental setting. Where available, the guidance links to case studies with analytical procedures described in detail. Available information is outlined in Annex 2.

1.5 Reference to other guidance under the Stockholm Convention

This guidance is part of a larger set of guidance developed to assist parties in developing, updating, and reviewing their implementation plans with information relating to the persistent organic pollutants listed in 2009 and 2011 (UNEP/POPS/COP.6/INF/15). Where appropriate, reference to this guidance is provided for further reading. A particular link exists to the Strengthening POPs Regulatory Framework Guidance, which concerns improving the regulatory framework for monitoring of newly listed POPs in articles and products. Useful information on analytical aspects of POPs can be found in the Guidance on the Global Monitoring plan for Persistent Organic Pollutants, recently updated with information relevant to the POPs listed in 2009 and 2011 (UNEP/POPS/COP.6/INF/31).

⁵ PFOS, polybrominated diphenyl ethers and pentachlorobenzene

1.6 Approach of presenting case studies

Where available, best practice case studies for key articles/products possibly containing POPs listed in 2009 and 2011 are referenced in the respective chapters and described in Annex 3. If possible, case studies or publications were selected with reports available in the public domain and the access information provided.

With the inclusion and link to a range of case studies on monitoring of POPs listed in 2009 and 2011 in articles and products in different countries/regions, the guidance endeavours to provide information on already performed studies, and the approaches used. These case studies can be assessed with the view of selecting the most appropriate approaches and methodologies (sampling and analysis). Some of the case studies reveal that many former applications of PFOS and PBDE are not relevant anymore e.g. in recent surveys PFOS and related substances were no more detected in coated paper (see below).

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2 General considerations and cross-cutting issues

2.1 Capacity building and accreditation

Laboratory personnel need to be trained on the different analytical procedures and methodologies for POPs monitoring and also on quality assurance and quality control (QA/QC). UNEP has within its activities related to the Global Monitoring plan for Persistent Organic Pollutants (GMP) a program on capacity building for POPs analysis (mainly for governmental laboratories), which could be considered. The programme is implemented in cooperation with the University Amsterdam/The Netherlands and the University Oerebro/Sweden. Furthermore capacity building on POPs analysis is offered by JAICA or in summer schools (e.g. by RECETOX, SC Centre Brno, Czech Republic).

For continuous education of laboratory personnel on general laboratory QA/QC, information resources such as dedicated books with training materials on QA/QC could be utilized.⁶ Furthermore, learning options available through the Internet (E-learning or Webinars) could be explored and assessed for their usefulness.

To develop own analytical methodologies laboratories might consider accreditation schemes such as ISO 17025.

2.2 General quality assurance and quality control (QA/QC) considerations

International and national standard procedures for the analysis of chemicals contain dedicated sections on QA/QC. Other measurement protocols often do not contain dedicated sections on QA/QC and, therefore, if no specific international or national standard procedures are available or used by a laboratory, at least the following common procedures for the quality assurance of quantitative analysis of POPs listed in 2009 and 2011 should be considered:

- cleaned laboratory equipment, material, and chemicals to be used to avoid contamination from background
- system ensuring that effectiveness of the measurements and procedures is continuously supervised through the analysis of procedural blank samples
- regular injection of solvent blanks and standard solutions
- tests to be carried out to evaluate the accuracy of the method, e.g. efficiency of the extraction methods, the recovery of the analytes, stability and loss of analytes in solution during storage, calibration using matrix matched standards or standard addition, and use of proper internal standards
- tests to be carried out to evaluate the precision (repeatability and reproducibility), the limits of detection (LODs) and quantification (LOQs), the robustness and the specificity of the whole method, from sampling to detection
- clearly defined criteria for identification and quantification need to be applied, and calibration curves to be used
- storage of analysed samples and data (including instrumental raw data) for a defined time

2.3 International standards for analysis of POPs

Where possible, links are made to existing international standards for analysis of a particular POP. However, for a number of article matrices no international standards are available for sampling,

⁶ E.g. Wencławiak, B.W., Koch, M., und Hadjicostas, E. (eds.): Quality Assurance in Analytical Chemistry - Training and Teaching. 2nd Edition, p. 247- 272, Springer-Verlag, Berlin Heidelberg 2010.

extraction and clean-up. E.g. a standard for measuring PBDEs in EEE (International Standard IEC 62321) in respect to RoHS compliance is under development and will probably become available by 2013. An international standard for extractable PFOS in articles and its analysis has been developed (NPR-CEN/TS 15968) but has not been validated yet. Furthermore, no (standard) analytical procedure is available for many of the 160 listed PFOS related substances including some non-extractable PFOS precursors.

Also for PeCBz or HCB the extraction from products like pigments cannot be performed appropriately with available CEN, ISO or EPA standards. Here standard extraction procedures of matrices with e.g. toluene (which is sufficient for most environmental matrices or for sampling adsorbents like PUF filters or XAD resins) do not necessarily lead to satisfying extraction efficiency or reproducibility for products and articles. The analysis of pigments for PeCBz/HCB and other unintentional POPs, therefore, needs specific extraction procedures, which are not described (yet) in international standards (see below).

The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of respective articles and mention their limitations for articles/products;
- Describe some standard methodologies used by laboratories experienced in the analysis of POPs listed in 2009 and 2011 contained in certain articles and products;
- Describe case studies with links to reports where monitoring or analytical procedures for a certain matrix are described.

For specific matrices, procedures and standards will further be developed. They could be considered during the updating of this guidance.

2.4 Step by step approach

To determine the occurrence and quantities of POPs in different articles, including consumer products, representative samples can be purchased from retail outlets and analysed.

A similar strategy can be used to determine the occurrence and quantities of PFOS and its related substances in other materials, such as the industrial materials used downstream in a product chain, consumer products, chemical formulas and industrial blends arriving at the borders and possibly identified by the customs or other competent authorities.

2.4.1 Step 1: Survey of products and articles containing POPs listed in 2009 and 2011

Before collecting samples, a survey can be conducted to determine the availability of articles that possibly contain or have been treated with POPs chemicals. Sample candidates can be identified from the list provided in Annex 1 for the respective newly listed POP. If access is easy then the team conducting the study might take samples. Relevant stakeholders for the different groups might be contacted for support and input and for samples.

2.4.2 Step 2: Sample collection

A sampling protocol is to be used and should contain the following information:

- Type of sample
- Location of sampling
- Any relevant information on the sample

The sample should be wrapped in aluminium foil and transferred into a vessel or container (e.g. glass or another inert material) with a cap or screw top. The vessel should be labelled (readable, persistent against solvents and water, with unique information e.g. code related to sampling protocol, if the sample represent any hazard this should be noted and the sample labelled respectively). The

collected samples should be stored adequately (e.g. appropriate temperature; possibly exclusion of light).

Specific care should be given to cross contamination of and in the laboratory, in particular if the laboratory also analyses other newly listed POPs in trace quantities (e.g. air samples). Procedural blanks, which are blanks that are treated exactly like the samples, provide good indication if there are background or crossover contamination. For PFCs special attention should be paid on contamination in solvents, in the elastomers in the HPLC instruments and in coated septa and filters. Furthermore long chain PFCs can adsorb fast and strongly to glass.

The pre-screening of samples can include specific approaches (see also Strengthening POPs Regulatory Framework Guidance):

- a) Considerations on the different use areas (see Annex 1-A)
- b) CAS numbers, chemical names or product names (see Annexes in Custom Control Guidance¹⁶).
- c) Certain risk criteria (e.g. importing company, receiving company or use for a specific purpose) or certain chemical properties or performance properties (e.g. stain repellent)
- d) If applicable, mobile screening methods can be used during the field sampling. Non-destructive methods can even be used for selections of samples in stores and shops. The sensitivity of the screening methodology should cover the regulatory limit for a newly listed POP for a certain sample category. E.g. mobile screening techniques for fluorine can detect fluorine concentration of approximately 0.1% (e.g. Sliding spark spectroscopy or certain XRF). If legislation requires that PFOS is detected below such a level (see e.g. the European legislation for carpets and textiles with a limit value of 1 µg PFOS/m²) then this screening methods cannot be used for pre-selection of samples for assessment of compliance with the limit value.

2.4.3 Step 3: Optional (further) screening in the laboratory

The sampled articles can be screened for the presence of e.g. fluorine or bromine in the laboratory, usually being more sensitive, compared to the mobile equipments used in the field. Screening methods have been developed, which allow determination of presence of the chemical in the sample (see e.g. the DART method described for PFOS and other PFCs or the pyrolysis GC/MS method for PBDEs and other BFRs) (see chapter 3 and chapter 4).

When screening methods are applied, it needs to be ensured that the detection limit of the screening method is more sensitive than the legislation limit required for the content of the chemical.

2.4.4 Step 4: Quantification

Usually quantification requires that the chemical is extracted from the sample and the extract subjected to a clean-up procedure. Extraction methods and the clean-up procedures should be validated and where available taken from standard norms. If own procedures are used they should have proven to lead to correct results and being robust against modifications in the sample matrix.

Finally instrumental analysis with appropriate sensitivity to achieve the required detection limits needs to be used for the data acquisition and quantification. Quantification is either done with internal standards (e.g. isotope labelled standards, such as carbon ¹³C-labelled chemicals for mass spectrometric detection) or other appropriate analytical standards, or by external calibration.

Different analytical methods are described or referenced in the respective sections. For most POPs an example of instrumental settings is described in Annex 2 in combination with a chromatogram.

2.4.5 Step 5: Documentation and reporting

The result of the screening would be documented in an appropriate form. The reporting might include the compilation of a report on the monitoring study including scope, samples, procedures, and results. The documentation could also include the publication in peer reviewed journals, which at the same time would be a further validation of the methodology used and the results.

The results would be communicated to the stakeholders concerned or interested (see Strengthening POPs Regulatory Framework Guidance).

2.5 Overview on instrumentation

Figure 2-1 gives an overview on the clean-up and analytical instruments used for an air sample by a commercial laboratory capable to analyse all listed POPs. For the initial listed 12 POPs all compounds could be measured with gas chromatography (GC) coupled to mass spectrometry (MS) and for basic pesticides or PCBs also by GC- Electron Capture Detector (ECD).

For two of the POPs listed in 2009 and 2011 (PFOS and Chlordecone), the use of liquid chromatography (LC) is required (see Figure 1).

Since the concentrations in products or articles are normally high (sometimes in percent range) compared to environmental samples, high resolution MS (HRMS) is not required for most of the article types to be screened but low resolution MS (LRMS) or ECD can be used. For some articles with low regulation limits more sensitive methods might be necessary (e.g. for PFOS in carpets or unintentionally POPs in food/feed).

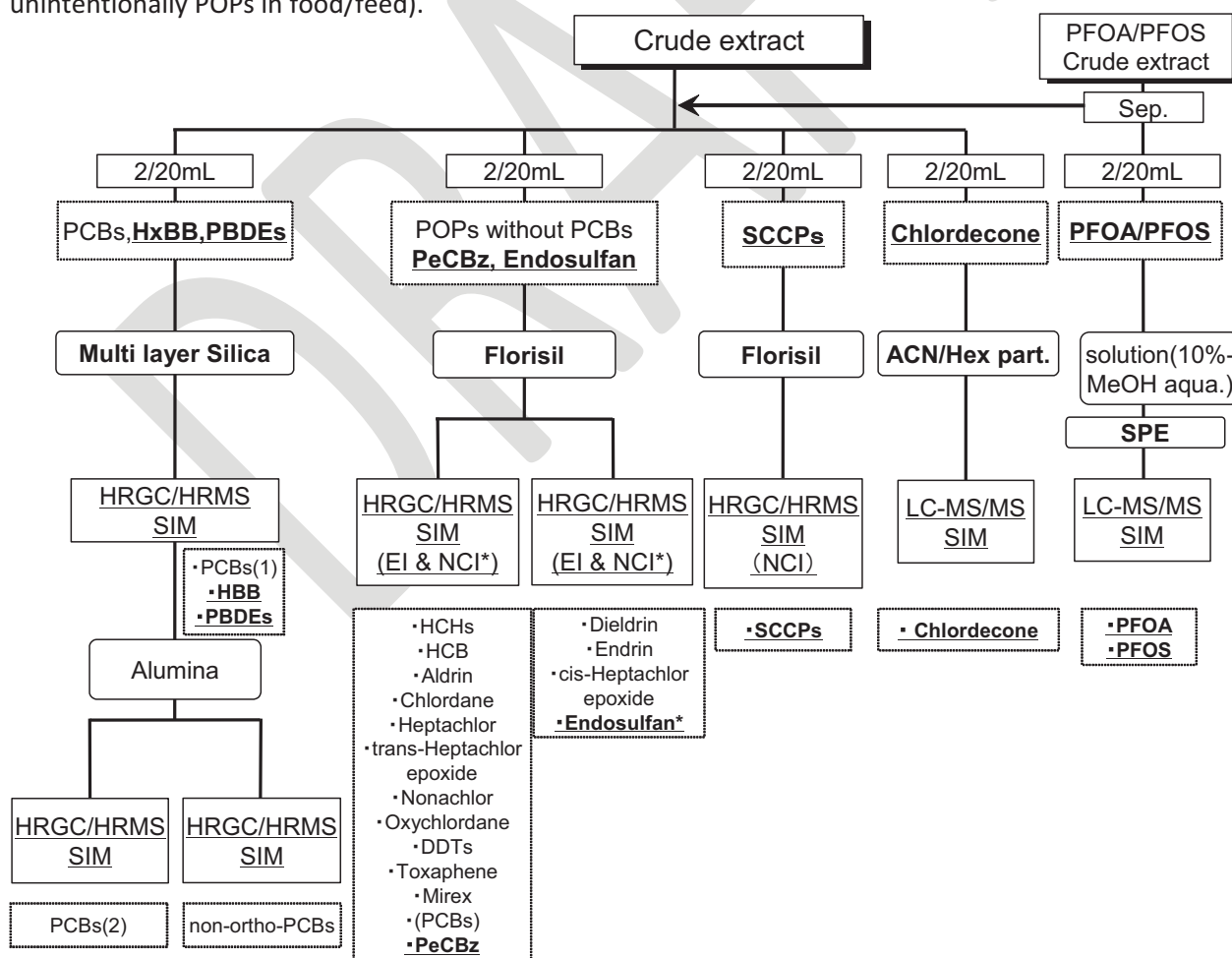


Figure 2-1: Clean up of an air sample and instrumentation for analysis of all listed POPs in air (courtesy Prof. Takumi Takasuga; Shimadzu Techno Research, Japan).

Please note: For analysis of air with low concentrations of POPs HRMS or sensitive LRMS is used, for analysis of newly listed POPs in articles low resolution GC or ECD is normally sufficient (see respective sections in this document).

DRAFT

3 Sampling, screening and analysis of PFOS and related substances in products and articles⁷

3.1 Products and articles possibly containing PFOS

A list of possible PFOS uses and those of related chemicals are given in Annex 1-A. The list contains applications in articles, which are included in specific exemptions or acceptable purposes as well as former uses and possibly impacted recycling flows. Also other potentially contaminated secondary articles from recycled materials or other contamination are mentioned. This list can be utilized for selecting samples for the screening.

A range of PFOS applications are within articles⁸ (e.g. specific fire fighting foams, chromium plating mist suppressants, pesticides) or used for coating of articles (e.g. carpets, textiles, furniture, paper). Several of these applications were granted specific exemptions or acceptable purposes and therefore such newly produced articles can still be traded at present. Furthermore a range of articles with long life expectancy formerly produced containing PFOS or related substances might be still in use (e.g. carpets, textiles, furniture and fire fighting foams).

The current PFOS and related substances use in China (the largest producer and user) is estimated to 100 tonnes mainly used for plating industry (30 – 40 t/y), specific fire-fighting foams (25 to 35 t/y) and sulfluramid insecticides (4-8 t/y) (Zhang et al. 2012)⁹.

3.2 Step by step approach for PFOS analysis in products and articles

The step by step approach for monitoring of POPs listed in 2009 and 2011 is described in 2.4. To determine the occurrence and quantities of PFOS and its related substances in different articles including consumer products representative samples can be purchased from retail outlets and analysed. A similar strategy can be used to determine the occurrence and quantities of PFOS and its related substances in other materials and wastes, such as the industrial materials used downstream in a product chain, consumer products and chemical formulas arriving at the borders and identified by the customs.

Step 1: Survey of products and articles possibly containing PFOS and related substances

Before collecting samples, a survey can be conducted to determine the availability of consumer products that contain or have been treated with fluorinated chemicals. Sample candidates can be identified from the list compiled in Annex A-1. Some case studies on PFOS and other per- and polyfluorinated chemicals (PFC) monitoring described below developed a survey approach. Relevant stakeholders for the different use groups might be contacted for support and input and for samples. Relevant stakeholders to be contacted for the different use categories are listed in Annex 1-A

Step 2: Sample collection

Samples can then be collected e.g. by the customs at the import or by competent authorities like factory control or consumer protection authorities and related institutions; see Custom Control

⁷ Please note: The analysis of PFOSF listed in the Stockholm Convention is only to a limited extent possible or useful since the compound is not stable in the environment, products and in most solvents (including water) and not used in articles/products. Instead PFOSF is only used as intermediate for the production of PFOS related substances. Therefore no analysis need to be described in this guidance for PFOSF and it should not be requested in tenders for monitoring of newly listed POPs or if analysis of PFOS and related substances is asked to a commercial laboratory.

⁸ A large part of PFOS containing substances have already been disposed to landfills. It is estimated that 200 to 1700 tonnes of the estimated 96000 tonnes (approximately 1%) have reached the ocean (Paul AG, Jones KC, Sweetman AJ (2010) A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ. Sci. Technol. 43, 386–392.)

⁹ Zhang L, Liua J (2012) The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China. Environmental Pollution 165, 193-198.

Guidance¹⁰ and Strengthening POPs Regulatory Framework Guidance¹¹. Sampling campaigns can also be conducted by research institutions.

Following criteria and information can be used by the stakeholders:

- a) The article contains PFOS and its related substances identifiable by the chemical names, CAS numbers or if their structural formulas contain more than three fluorine atoms; or
- b) The article contains fluorinated chemicals identifiable by their trade names; or
- c) The article was identified as having certain properties that are common for articles treated with PFOS and its related substances (e.g., stain resistant, water repellent and anti-grease), as can be identified with e.g. the Droplet test.

Step 3: Screening for presence of fluorine and of fluorinated organic chemicals

Sampled articles can be screened for the presence of fluorine to exclude those with false claims and those that achieved certain surface properties (e.g., anti-grease) without using fluorinated chemicals. Typically, 0.05 to 0.5% of the PFC by weight¹² of the article is used to ensure durable repellence. Thus, samples containing 0.01% cut-off are included for further analysis, provided an adequate safe margin to ensure that all sample articles treated with fluorinated chemicals are included. Sample articles containing less than 0.01% fluorine by weight can therefore be discarded if not specific legislation require that PFOS is below such a level (see e.g. the European legislation for carpets and textiles). In this case screening, methods cannot be used for a pre-selection of samples.

The fluorine content can be determined by using wavelength dispersive (WD) X-ray fluorescence (XRF) spectrometry. Instrument and operating parameters for this method are provided in Table 8. XRF might also be useful as a screening method for fluorinated substances in waste or products but the known limitations of the method are low sensitivity and lack of structure-specific information. Furthermore more sophisticated screening in laboratory with DART, DESI and ¹⁹F NMR (see below) can be applied.

Step 4: Quantification

Different analytical methods can be applied as e.g. described in Annex 2-D. Some methods have been described in more detail in national surveys with quantifications of PFOS and other PFCs in consumer products (see e.g. [USEPA 2009](#)¹³ or SWEREA 2004¹⁴).

3.3 Screening methods for fluorine/organofluorine chemicals

3.3.1 Introduction

For a pre-selection of samples, screening methods for PFOS/PFCs are valuable. Most of such screening methods cannot identify specifically PFOS but need then a confirmation analysis for PFOS and other PFCs by MS methods (see below).

¹⁰ Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft).

¹¹ Stockholm Convention (2012) Strengthening POPs Regulatory Framework Guidance (Draft).

¹² For articles made of polytetrafluoroethylene (PTFE), such as thread sealant tape, Teflon tubing and some dental floss, the fluorine content can be greater than 70%.

¹³ USEPA 2009. Perfluorocarboxylic acid content in 116 articles of commerce. U.S. Environmental Protection Agency, March 2009.

¹⁴ Swerea 2004. Survey, screening and analyses of PFCs in consumer products. Dorte Herzke, Stefan Posner and Elisabeth Olsson. Swerea IVF project report 09/47. Climate and pollution agency in Norway, TA-2587/2009.

Some of the screening methods can (semi-)quantify the organofluorine content. Such a measurement might be valuable in cases where PFOS is partly chemically bound or where a larger part of PFOS is present as PFOS precursor for which no analytical standard method exists.

Most screening tools provide only poor semi-quantitative information. In case of spectroscopic approaches (WDXRF, SSS) only fluorine present at the sample surface is detected and semi-quantified.

In case of GC-EPED (Echelle-Plasma-Emission-Detector) coupled to a headspace or a purge & trap sampler, mostly volatile precursors of PFOS are detected and levels of precursors do not necessarily give robust hints on PFOS levels. Fluorine ^{19}F NMR is a quite sensitive screening technique (LODs around 300 ng/mL solution), which can distinguish fluorine chains bound to different functional groups, such as sulphates, phosphates, acrylates and ethers (Trier 2011, Ellis 2004). Another option is to make extracts of the sample, and screen for PFCs by accurate, high resolution mass spectrometry (LC-HRMS) by searching for a combination of 1) typical negative mass defects, 2) homologue series separated by 50 Da or 100 Da 3) typical perfluorinated ions (for perfluorinated compounds, such as PFOS) and/or 4) specific neutral losses, such as HF (for polyfluorinated PFCs containing hydrogen). This methodology has been used to screen industrial blends and paper extracts with (Trier 2011) typical CnFm fragments (i.e. m/z 119, 131, 169, 195, 231, 331).

3.3.2 Screening with the “drop test”

When PFOS or other PFCs are coated on a textile substrate and exposed to water (surface tension of 72 mN/m) or oily substances (surface tensions of 20 mN/m and more), they will not spread on the textile surface (Posner 2011). This phenomenon is called “water and oil repellence” and used for water, oil and stain protection of carpets, textiles or leather.

Most alternatives cannot achieve a surface energy lower than 22 mN/m or lower, the surface energy for oil (Posner, 2011). Materials with a high contact angle and low surface energy are therefore likely treated with perfluorinated substances. Highly fluorinated surfaces can be distinguished from non-fluorinated surface treatments, if both a droplet of water and a droplet of oil put on the surface form pellets. If the oil droplet flattens out, the surface is likely treated with a non-fluorinated chemical (hydrocarbon surfactant or a silicone coating). The spreading of a liquid on a surface demonstrates when a fabric is being treated or not by the degree of wetting measured by the contact angle (Figure. 3-1 and 3-2). Contact angle, θ , is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect as shown in figure 3-2. It can be seen from this figure that a low values of contact angle (θ) indicates that the liquid spreads, or wets well, while a high contact angle indicates poor wetting. If the angle θ is less than 90 degrees the liquid is said to wet the solid. If it is greater than 90 degrees it is said to be non-wetting. A zero contact angle represents complete wetting (Posner 2011, Kissa 2001).

The wetting angle can be used for screening of PFOS (and other PFC) treated materials.

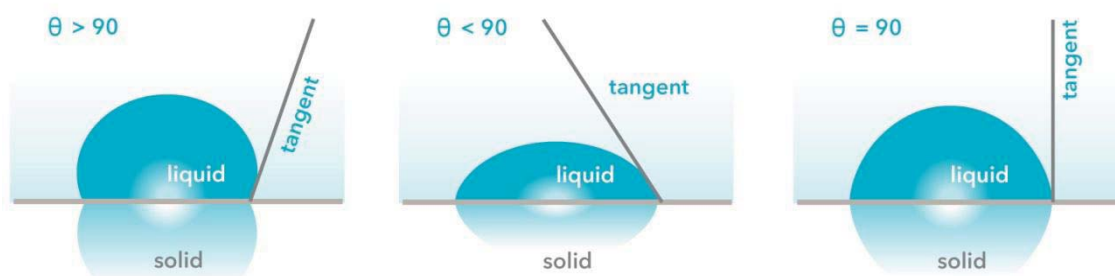


Figure 3-1: Contact angle θ categories of a droplet on a surface

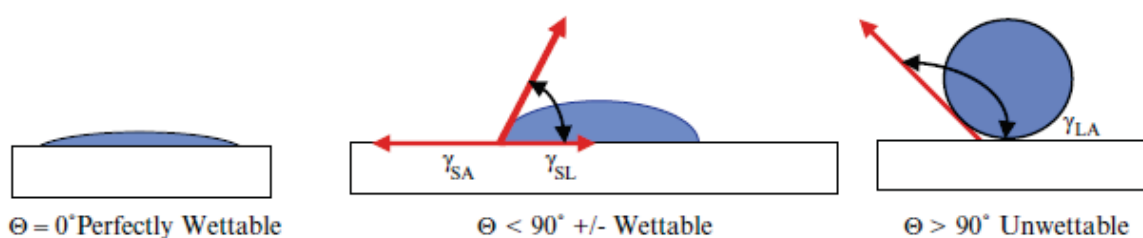


Figure 3-2: Contact angle versus wettability of a substrate surface. When angle Θ is $> 90^\circ$, liquid will not wet the surface; when angle Θ is $< 90^\circ$, liquid will wet surface partially; when angle $\Theta = 0^\circ$, complete spreading & wetting of the surface by the liquid. Spreading occurs only if $S > 0$. Spreading coefficient: $S = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL})$ (Posner 2011; S = solid, L = liquid, A = air. where γ_{SA} = surface energy of the substrate (e.g., polymer surfaces), γ_{LA} = surface tension of the liquid and γ_{SL} = interfacial tension).

3.3.3 Screening of Fluorine with WD-XRF-Analysis

Wavelength dispersive XRF (WD-XRF) systems are able to detect fluorine in vacuum mode. Respective systems (e.g. S8-TIGER; Bruker AXS, Karlsruhe) are used to analyse products and articles on their fluorine content. It is important to understand that for fluorine the depth of signal saturation is limited to the first micrometers, caused by the very low energy of the obtained fluorescence radiation. Applying the WD-XRF of Bruker to the fluorine screening in coated papers an LOD of 0.05% fluorine was elaborated. Taking into account, that per- or polyfluorinated side groups of large coating molecules are expected to form the outer shell of the sample matrix, the LOD of 0.05% is sufficient for perfluorinated structures ($-C_nF_{2n+1}$). If the depth of saturation reaches the non-fluorinated backbone structure of the coating molecules also, the LOD of 0.1% might be too high for very thin coatings or those containing only low levels of fluorine.

Table 2-1: WD-XRF method and operating parameters for screen-testing samples for the presence of fluorine (USEPA 2009)

Instrument	Panalytical PW2404 Wavelength Dispersive (WD) X-ray Fluorescence (XRF) Spectrometer equipped with the PW2540 Sample Changer
Software	SuperQ (Panalytical) for instrument control IQ+ (Panalytical) for calibration and quantification
Power of X-ray tube	4000 watts
Measurement atmosphere	Vacuum (< 10 mb) or under helium atmosphere
Scan method	A continuous scan mode followed by fluorine-specific data

	collection at the peak fluorine wavelength for an additional 10 second measurement.
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^a

Liquid samples were tested on filters by wetting a 47-mm paper filter (Whatman) with approximately 0.5 mL sample, and then air drying the filter under an aluminum foil cover.

3.3.4 Fluorine screening with ¹⁹F NMR spectroscopy (Trier 2011¹⁵, Ellis et al. 2000¹⁶)

Fluorine has an uneven number of protons, and hence has an unpaired proton with spin ½, which couples electromagnetically upon being exposed to a magnetic field. Fluorine is furthermore monoisotopic, and has a high sensitivity (81% compared to Hydrogen). This, together with the high numbers of fluorine present in PFOS and other PFCs, makes ¹⁹F NMR a sensitive screening technique, capable of screening down to approximately 300 ng/mL (ppb) in samples of e.g. paper and board (Trier 2011).

Extracts of samples, containing no particulates, are made with organic solvents and evaporated down to approximately 100 µL, and redissolved in deuterated solvent (e.g. MeOD), so that max. 10% of the solvent is hydrogenated (e.g. H₂O or MeOH). The samples are analysed on an NMR instrument (minimum 500 MHz) equipped with a dual H-F probe, and scans up to 24 hours are acquired. Cr(III) acetate is added as relaxation agent, and an internal standard with chemical shifts of the PFOS or other PFC analytes is added too (Ellis et al. 2000; Trier 2011). The screening can be made semi-quantitative, and is capable of detection unknown organofluorines. The instrumentation is highly specialised, costly and immobile.

3.3.5 Screening of Fluorine: Sliding spark spectroscopy (Wolz et al. 2011)¹⁷

The basic principle of the method is the thermal vaporization of a small amount of the sample surface using a train of defined high-current sliding sparks (Seidel et al., 1993)¹⁸. The material components in the spark plasma are vaporized, atomized and activated to emit radiation. Software analysis of the delivered spectra gives information on the content of elementary fluorine on top of the surface. For fluorine a typical double-peak at a wavelength of about 350 nm is obtained. In defining special hardware setup, it is possible to get the absolute intensities of the fluorine emission line. The measurement is repeatedly done at different sites of the sample surface. The system is mobile and can detect organofluorine (as PFOS) at a concentration of approximately 0.1%.

3.3.6 Screening of Fluorine: P&T-GC-EPED (Wolz et al. 2011)

A Plasma Emission Detector with Echelle Spectrometer (EPED, IMT Innovative Messtechnik GmbH) coupled with gas chromatography (AG6890, Agilent) and a purge & trap sampler (PTA3000, IMT, Moosbach) can also be used for screening of volatile organofluorine compounds. The EPED detector combines a long term stable pulsing plasma cell with a high resolution Echelle spectrometer. The resulting multi-element gas chromatographic detector shows high sensitivity and selectivity for sulphur and the halogens chlorine, bromine, fluorine and iodine with detection limits for the above

¹⁵ Trier X (2011) Polyfluorinated surfactants in food packaging of paper and board. PhD Danish Technical University, Copenhagen/Denmark.

¹⁶ Ellis DA, Martin JW, Muir DCG, Mabury SA (2000) Development of an ¹⁹F NMR Method for the Analysis of Fluorinated Acids in Environmental Water Samples Anal. Chem. 72, 726-731.

¹⁷ Wolz G, Gruber L, Fiedler D, Schlummer M (2011) Development of screening methods for fluorinated coatings of food contact materials and other everyday commodities.

http://www.ivv.fraunhofer.de/no_html/gf3_29.pdf

¹⁸ Seidel T, Golloch A, Beerwald H, Böhm G, (1993) Fresenius' Journal of Analytical Chemistry 347, 92-102.

elements < 10 pg/s corresponding to approx. 100 pg¹⁹ (peak width of 10 sec) and a linearity about 3-4 orders of magnitude. The equipment is stationary in laboratory and not mobile.

3.3.7 Screening of PFOS and related substances: HS-GC-EI-MS or HS-GC-CI-MS

A more sophisticated screening tool is a headspace sampler connected to a GC-MS system. About 1 dm² of the material is placed into a 10 ml headspace vial. At a temperature of 150°C volatile PFOS precursor compounds are released into the headspace. An aliquot of the headspace volume is transferred onto a GC column and detected by EI-MS after chromatographic separation. Typical CnFm fragments (i.e. m/z 119, 131, 169, 195, 231, 331) are then monitored in order to identify the presence of organofluorinated compounds. If run with chemical ionisation even molecular ions can be detected enabling an identification of the detected PFC.

The equipment is stationary in laboratory. It allows a high throughput of samples for screening of volatile PFOS precursors.

3.3.8 Screening of PFOS and related substances in articles with DART-TOF MS

The Direct Analysis in Real Time (DART) - Time of flight (TOF) mass spectrometer (DART-TOF MS) couples the DART ion source with the high-resolution, accurate mass capability of a time-of-flight (TOF) mass spectrometer.

The sample is placed in its native form between the DART ion source and the TOF mass spectrometer inlet. The DART source ionises the sample. Typically no solvents or sample preparation are required. With DART MS chemical composition is determined and high-resolution accurate mass spectra are produced.

While the technology has been applied for screening of PFCs on paper (DiPAPS up to 1500 Dalton) (Ackerman et al. 2009)²⁰ there is currently no monitoring of PFOS and precursors reported, partly due to the specialised ionisation device/cost of this method.

3.3.9 Screening of PFOS and PFCs in articles with accurate mass by HRMS

Filtered extracts can be screened for the presence of organofluorines (soluble in LC eluents) by high-resolution, accurate mass (Quadrupole) Time-of-flight (TOF) mass spectrometry. The search starts with a screening for 1) typical negative mass defects, i.e. the ions have m/z just below nominal mass, e.g. 412.99 instead of 413.00. The m/z of the suspect compounds is then used to make EICs (extracted ion chromatograms) to see if they belong to a homologue series separated by 50 Da or 100 Da. The spectra can also be checked for the presence of 3) typical perfluorinated ions (CnFm fragments (i.e. m/z 119, 169, 219, 269, etc. – these ions are prevalent for perfluorinated compounds, such as PFOS) and/or 4) specific neutral losses, such as HF (loss of n times HF (20 Da), i.e. look for losses of 20, 40, 60, 80 Da – typical losses for polyfluorinated PFC containing hydrogen).

This methodology has been used to screen industrial blends and paper extracts (Trier 2011). The method is fast, simple and specific, but the instrumentation is costly and not mobile.

¹⁹ 100 pg may be purged from 10 ml of extract from 0.5 g of coated paper corresponding to 200 pg/g paper.

²⁰ Ackerman LK, Noonan GO, Begley TH (2009) Assessing direct analysis in real-time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 26, 1611-1618.

3.4 Qualitative and quantitative analysis of PFOS and related substances

3.4.1 Background and general challenges of PFOS/PFC analysis

Analytical standard methods for quantification of PFOS and other PFCs are under development, and very few technical standards have been defined (see table 3-1; and section 3.5.2). Due to their relative low volatility, good solubility in water and lack of chromophores the analysis of perfluorinated alkyl substances is a challenging task. The analytical problems associated with the determination of neutral and anionic PFCs are multiple, and include diverse aspects such as unique physico-chemical properties, lack of reliable standards, degradation of standards, impurities, complicated mixtures of isomers and congeners, adhesion of the analytes to the analytical equipment, ion suppression, and contamination during all stages of the analytical procedure, including instrumental sources. When using the different available analytical methods for PFOS and its related substances caution should be given to follow the measures needed to assure that they provide reliable results. The challenges connected with quantification methods for PFOS and its related substances are described in the literature (Martin et al. 2004)²¹.

The analytical detection method of choice for PFOS and most PFCs is currently [LC-MS or LC-MS/MS](#) for the anionic compounds (including PFOS and PFOA), whereas both LC-MS(MS) and GC-MS can be used for the determination of the neutral per- and poly-fluorinated alkylated substances including several precursors of PFOS. Quadrupole tandem mass spectrometry applying negative electrospray ionisation interfaces (HPLC/ESI-MS/MS) seems to be the preferred instrumental method for the determination of ionic PFCs. Recently also atmospheric pressure photo ionisation (APPI)-LC-MS/MS has been reported to give good ionisation of neutral fluorotelomer alcohols (FTOH). In LC-MS of anionic PFCs, usually the dissociated acid (pseudo molecular) ion $[M-H]^-$ is observed, which can be used for quantitative purposes in LC-single quad MS, or as the precursor ion for multiple ion reaction monitoring in LC-MS/MS. Detection limits of LC-MS(MS) and GC-MS methods are sufficiently low to allow in principle for the determination of environmental levels of PFCs in drinking water and in food samples if a country decides to include them in the monitoring.

Quality assurance measures are required to ensure best possible quality of the data. Liquid samples are diluted and extracted for both volatile and ionic compounds, followed by a cleaning step with activated carbon. Solid samples are homogenized prior to extraction and then treated similar to liquid samples.

Since PFOS and its related substances occur in a large range of materials and liquids, it is advisable to use skilled and specialized laboratories where accreditation is one efficient way to verify these skills. A list of laboratories accredited for analysing POPs and using Good Laboratory Practices (GLP) can be found in (<http://www.chem.unep.ch/gmn/gmnlabs/default.htm>).

It has to be underlined, that LC-MS systems have to be [especially prepared for PFOS/PFC analysis](#), due to blank issues related to fluorinated compounds in LC systems (e.g. from teflon parts). In addition, there are further important issues required for a reliable PFC analysis:

- a) use of specific standards for target analytes (not available for most PFOS precursors, mixed chain length PFCs and structural isomers)
- b) use of labelled internal standards (at least for the main target analytes)

²¹ Martin JW, Kannan K, Berger U, de Voogt P, Field J, Franklin J, Giesy JP, Harner T, Muir DCG, Scott B, Kaiser M, Järnberg U, Jones KC, Mabury SA, Schroeder H, Simcik M, Sottani C, van Bavel B, Kärrman A, Lindström G, van Leeuwen S. (2004) Analytical challenges hamper perfluoralkyl research. *Env. Sci. & Tech.* 38, 248A–255A.

- c) purity and stability of the standards. PFOSF, and probably a range of other PFOS precursors including e.g. esters (e.g. polyfluoroalkyl phosphoric acid esters (PAPs)) are prone to degradation (hydrolysis) if stored in alcohols/waters

Both volatile and non-volatile PFOS precursors and other PFCs are analysed using well established analytical methods applying GC/MS and LC/MS techniques. Quality assurance measures are required to ensure best possible quality of the data. Liquid samples are diluted and extracted for both volatile and ionic PFCs, followed by a cleaning step with activated carbon. Solid samples are homogenized prior to extraction and then treated similar to liquid samples. All calculated concentrations are either given in [µg/L] for liquids, [µg/kg] for solid materials or in [µg/m²] for textiles, paper and leather. Since PFOS/PFCs occur in a large range of materials and liquids, it is advisable to apply skilled and specialized laboratories where accreditation is one efficient way to verify skills.

3.4.2 Specific challenges with the analysis of PFOS precursors and bound PFOS

Analysis of PFOS precursors in articles

The OECD has developed a list of 165 PFOS related substances. Only for a few of these related substances a standard analysis is available (Table 3-2). Therefore currently most PFOS related substances are not covered by the standard analysis. While for environmental samples this might be of minor relevance due to degradation of these precursors to PFOS (e.g. frequently observed in sewage treatment plants where the PFOS concentrations mass balance of higher PFOS levels in sludge and outflow compared to the inflow). However in products and on articles PFOS precursors might be used which are not detected then by the routine PFOS analysis or state-of-the-art analysis including several PFOS precursors (Table 3-2).

Analysis of chemically bound PFOS

The current available standard to analyse PFOS in articles focus on the extractable PFOS (NPR-CEN/TS 15968; see below). In some applications, however, the PFOS related substances are chemically bound to the surface. Therefore the analytical standard procedures extract the extractable PFOS and PFOS related substances not bound to the surface. The largest part of chemically bound PFOS precursor could remain on/in the article leading to a considerable underestimation of PFOS related substances in these products.

3.4.3 Selected international standards for PFOS analysis

NPR-CEN/TS 15968²²

The NPR-CEN/TS 15968 standard is currently the only existing international standard for the determination of the extractable content of PFOS in solid items (e.g. textiles, leather, paper) and in chemical products (AFFF, cleaning agents, etc.) within the scope of supporting the EC Regulation 850/2004 on persistent organic pollutants (POP). An international standard has been developed here for "Determination of extractable perfluorooctanesulphonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LCqMS or LC-tandem/MS".

The method is currently a technical specification (TS) meaning it is not fully validated. In order to become a full European standard (EN) some further work needs to be done to ensure accuracy in analytical results with data from proficiency testing.

²² Preview of NPR-CEN/TS 15968 content: <http://www.evs.ee/preview/cen-ts-15968-2010-en.pdf>

As state in the name of the standard, the method only addresses the extractable PFOS and a few PFOS precursor (see table 9). The standard does not address the chemically bound PFOS related substances and also does not describe a holistic analysis of PFOS related substances.

It is applicable to concentrations of PFOS in the extract solution in the range between 0.5 µg/L and 50 µg/L.

ISO Method for water (ISO 25101:2009)

Currently no ISO standard is available to measure PFOS and other PFCs in articles or products. The only ISO standards for PFOS is ISO 25101:2009, which specifies a method for the determination of the linear isomers of PFOS and PFOA in unfiltered samples of drinking water, ground water and surface water (fresh water and sea water) using high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). According to the standard other isomers may be reported separately as non-linear isomers and qualified as such. The method is applicable to a concentration range of 2.0 ng/L to 10000 ng/L for PFOS and 10 ng/L to 10000 ng/L for PFOA. Depending on the matrix, the method may also be applicable to higher concentrations up to 200,000 ng/L after suitable dilution of the sample or reduction in sample size.

USEPA Method 537²³

USEPA Method 537 is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of PFOS and other selected PFCs in drinking water. The method has open access. The standard contains useful approaches on blank test, calibration, recovery etc. where reference is made in respective sections in this guidance.

²³ USEPA Method 537; http://www.epa.gov/microbes/documents/Method%20537_FINAL_rev1.1.pdf

Table 3-1: Summary of a survey on standardized analytical methods and methods reported in literature to be considered for PFOS analysis in mainly environmental matrices (Please note that the standard for analysis of extractable PFOS in articles NPR-CEN/TS 15968 - have meanwhile been developed and published, see below²⁴)

Method	Matrix	Extraction	Clean-up	Detection	Congeners/Standards	Limits of method	Reference
Standard methods for determination of polyfluorinated substances in water							
E DIN 38407-42:2010-05 (D)	Water	SPE	No details available	LC-MS/MS	Polyfluorinated substances	No details available	[DIN 2010]
EPA 537	Drinking water	SPE	-	LC-MS/MS	perfluorinated alkyl acids (incl. PFOS)	1.4 µg/L (DL) 6.5 µg/L (lowest concentration minimum reporting level)	[EPA 2009]
ISO 25101:2009	Water	SPE	-	LC-MS/MS	PFOA and PFOS	2,0 ng/l to 10 000 ng/l	[ISO 25101]
Standard method for determination of PFOS under development							
FprCEN/TS 15968	Coated and impregnated solid articles, liquids, fire fighting foams	Depending from matrix – no details available	Depending from matrix – no details available	LC-MS/MS; LC-MS	PFOS	0,5 ng/ml to 50 ng/ml in extract	[CEN 15968]
Methods for determination of PFOS its salts and PFOA in different matrices reported in scientific literature							
Literature	Water	On-line extraction (turbulent flow chromatography)	-Column wash	LC-APPI/MS	PFOS	18 ng/L (LOQ)	[Takino et al., 2003]
Literature	Waste water STP sludge	Sedimentation, decantation Solvent liquid extraction after drying and grinding (aqueous acetic acid and MeOH)	SPE (OASIS HLB)	LC-APPI/MS	PFOS	2.5 ng/L (LOQ) 10 – 25 ng/g (LOQ)	[Sinclair and Kannan., 2006]
Literature	Water, waste water	Filtration	SPE mixed hemimicelle-based	HPLC-ESI-MS/MS	PFAs incl. PFOS	0.2 ng/L (LOD)	[Zhao et al., 2007]
Literature	Sediment, sludge	Solvent liquid extraction (aqueous acetic acid and MeOH)	SPE	HPLC-ESI-MS/MS	PFAs incl. PFOS	0.1 µg/kg (LOD sediment) and 0.9 µg/kg (LOD sludge)	[Higgins et al., 2005]
Literature	Sewage sludge	Freeze drying, Soxhlet extraction, hot vapour extr., PLE	-	HPLC-ESI-MS/MS GC–NCI-MS	PFSAs incl. PFOS	6.000 – 10.000 ng/g (LOD) 10.000 – 20.000 ng/g (LOQ)	[Schröder 2003]
Literature	Dust	Solvent liquid extraction (MeOH) sonication	Centrifugation, filtration	HPLC-ESI-MS/MS	PFSAs incl. PFOS	10 – 50 ng/g (LOQ)	[Moriwaki et al., 2003]
Literature	Dust	Solvent liquid extraction (AcN) sonication	Centrifugation, SPE (C18)	HPLC-ESI-MS/MS	PFSAs incl. PFOS	0.99 – 4.56 ng/g (MDL)	[Kubwabo et al., 2005]

3.4.4 Sample pre-treatment

NPR-CEN/TS 15968 proposes grinding of samples to ensure an efficient extraction process without stating particle sizes. As in solid samples PFOS and related compounds are predominately found on the sample surfaces, a particle size of <1mm may be sufficient. However, for samples, which cannot easily be ground like paper, textiles, or leather, the technical standard recommends cutting leather (and textiles) into pieces of max. 25 mm², whereas for paper a max size of 1 cm² is given.

3.4.5 Extraction

Solid samples

In most cases methanol (MeOH), ethanol or acetonitrile (ACN) as well as mixtures of these solvents with water were chosen as extraction solvents for products. Clean-up is mostly achieved by solid phase extraction (SPE) on reversed phase C18 or WAX columns, which also reduces the presence of ion suppressing inorganic salts/minerals in the extracts.

Extraction techniques reported in these cases include ultrasonic assisted solvent extractions, accelerated solvent extractions (ASE), pressurised liquid extraction (PLE). With these techniques, typically 0.5 to 3 gram of sample matrix is extracted in 2-3 extraction cycles.

²⁴ Determination of extractable perfluorooctanesulphonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LC-qMS or LC-tandem/MS

Using ASE or PLE Teflon-free tubing and sealing are recommended (special care of the maximal allowed temperatures for the applied sealing materials is necessary). The ground (e.g. by cryohomogenisation, which makes most polymers brittle) or cut samples are mixed with MeOH pre-washed sea sand or comparable bulk materials and placed into the extraction cartridges. ASE or PLE is then performed at 80-100 °C, for 10-30 minutes per cycle (depending on sample types. The lower the diffusion coefficients of the sample matrix the longer the extraction times).

Ultrasonic extraction is performed with 10-30 ml of extractions solvent (ACN, MeOH) in polypropylene centrifugation tubes. Ultrasonic treatment takes 15-60 minutes (depending on sample type and particle size) and after a centrifugation step the supernatant is removed from the sample. The treatment is repeated once or better twice and the supernatants are combined.

If no clean-up is performed, the final extract is filtered (e.g. syringe filters of cellulose mixed ester (CME)) and reconstituted in MeOH/H₂O (1/1; vol/vol).

Liquid samples (e.g. AFFF, impregnation spays)

Liquid samples are usually diluted with water, a polar organic solvent (MeOH, ACN) or a mixture of both. If LODs greater than 100 µg/L are required, 1:100 (or even higher) dilutions of AFFF can directly be subjected to LC-MS. Lower LODs may be reached by prior clean-up with SPE columns. However, it is highly recommended to produce 1:100, 1:1000 and 1:10000 dilutions, and to start the LC-MS analysis with the highest dilution. This approach enlarges the operating times of the LC-MS system and prevents a PFOS overload.

The diluted sample is filtered (e.g. syringe filters (CME)) and reconstituted in MeOH/H₂O (1/1; vol/vol).

3.4.6 Clean-up

Three clean-up procedures can be recommended for PFOS and other perfluorinated carboxylates, phosphates and sulfonate acids. For challenging matrices combinations of these may be applied as well. Descriptions of extractions of neutral PFOS-precursors or volatile PFCs such as FTOHs can be found elsewhere, e.g. Benskin et al. 2012²⁵.

A fast and easy clean-up makes use of powders of activated carbon (e.g. Envicarb), which are applied to the sample directly, adsorb interfering matrix components and finally removed from the extracts by filtration (e.g. CME syringe filters) and/or centrifugation. Alternatively, sample extracts are subjected to SPE columns with active carbon. The cleaned extract is then eluted from the column with a suitable solvent (e.g. MeOH, ACN). The approach is applicable to all kinds of extracts (MeOH, ACN, mixtures of both with water, Methyl tert-butyl ether (MTBE)).

Secondly, extracts in MeOH or ACN are diluted with 5-10-fold amounts of HPLC water and subjected to SPE columns containing C₁₈ or weak anion exchangers. The SPE columns are prepared with 1 SPE volume of methanol and another of water, before the diluted sample is loaded onto the column head. The SPE column is then washed with water (adjusted to pH 4-6), MeOH/water, and/or THF/ACN/MeOH. Finally, PFOS and other perfluorinated carboxylates and sulfonate acids are eluted with 1-2 column volumes of methanol (adjusted to pH 10 with NH₃).

MTBE extracts from ion-pair extractions can be cleaned with florisil columns (100-1000 mg) prior to solvent change to methanol/water. Florisil columns are pre-washed with MeOH and MTBE before the sample is loaded. After washing with MTBE, target compounds are eluted with 30/70 MeOH/MTBE mixture (vol/vol).

²⁵ Benskin JP, Ikonomou MG, Gobas FA, Woudneh MB, Cosgrove JR. (2012) Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments. Environ Sci Technol. 46, 6505-6514.

In all cases, the eluents are filtered (e.g. syringe filters (CME)) and dried under nitrogen before reconstitution in MeOH/H₂O (1/1; vol/vol).

3.4.7 Calibration

Calibration standards are normally produced by commercially available mixtures of native and isotope labelled perfluorinated carboxylates and sulphonates and are used for calibration. Isotope labelled analytes are only relevant when mass spectrometry is used for detection. EPA 537 suggests that at least five calibration concentrations are required to prepare the initial calibration curve spanning a 20-fold concentration range and that larger concentration ranges will require more calibration points.

Note, that PFCs are prone to matrix enhancement when analysed by LC-Electrospray ionisation (ESI)-MS, why it is advised that either matrix matched or standard addition calibration curves are used. External calibration curves and precursors for which no native and/or internal standards exist should be used with great care for interpretation.

An example for detailed requirement on calibration is described in the EPA 537 methods. These include e.g. the demonstration and documentation of acceptable initial calibration before any samples are analyzed. After the initial calibration is successful, a continuing calibration check is required at the beginning and end of each period in which analyses are performed.

3.4.8 Recovery

According to NPR-CEN/TS 15968 the check of analyte recoveries can be performed by two differently isotope labelled PFOS or PFOA standards. The internal standard applied for quantification is added to the sample at the beginning of the analytical procedure, whereas the other (recovery standard) is added to the final cleaned and volume reduced extract. The alternative way to check recoveries is the fortification of samples with native PFOS.

The EPA Method 537 requires a surrogate recovery in the range of 70-130%, which seems a reasonable approach. If the recovery is out of this range the method also suggest steps to check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. Then to correct the problem and reanalyze the extract.

3.4.9 Blank measurements

As a minimum quality assurance, method blank samples are required. The procedural blank shall be at least threefold less than the limit of quantification of the method. Blank samples are treated in the same way as the samples, but do not contain sample matrix. For ultrasonic extracts, the normal volume of extraction solvent (MeOH, ACN) is used, with ASE or PLE cartridges filled with sea sand or a comparable bulk material is used. For ion pair extractions or liquids, HPLC water is used as substitute in method blank samples. Note that ultrasonic extraction risk to decompose labile PFC precursors, e.g. esters.

If PFOS levels in method blank samples increase, it is recommended to compare these with levels in pure solvent blanks, i.e. ACN/water (1/1; vol/vol) or MeOH/water (1/1; vol/vol) or pure HPLC water. This helps to distinguish between solvents or bulk materials as a major source of contamination. Polypropylene tubes and sample containers can be reused, however, are discarded after samples with increased PFOS levels had contact to their surfaces. High concentrated PFOS extracts or solutions can migrate into the plastic walls and cross contaminate low concentrated samples or extracts.

3.4.10 PFOS and selected PFOS related substances monitored

In table 3-2 PFOS and related substances, which can be considered to be part of state-of-the-art analysis of PFCs are included. However as mentioned above, most of the 165 PFOS related

substances are not covered by the current used state-of-the-art analysis. In table A6.-2 in the Annex also other PFCs are listed which are covered by state of the art analysis.

Table 3-2: PFOS, PFOS related substances included in state-of-the-art monitoring. (from 165 PFOS related substances; *Analytes listed in CEN/TS 15968:2010).

Abbreviation	Full name	CAS #	Detection method
Fluorooctane sulfonamides/ sulfonamidoethanols			
PFOSA*	Perfluorooctane sulfonamide	754-91-6	LC-MS
N-Me-FOSA*	N-Methyl-heptadecafluorooctane sulfonamide	31506-32-8	LC-MS
N-Et-FOSA	N-Ethyl-heptadecafluorooctane sulfonamide	4151-50-2	LC-MS
N-Me-FOSE*	N-Methyl-heptadecafluorooctane sulfonamidoethanol	24448-09-7	LC-MS
N-Et-FOSE*	N-Ethyl-heptadecafluorooctane sulfonamidoethanol	1691-99-2	LC-MS
Perfluoro sulfonates			
PFOS*	Perfluorooctane sulfonate	1763-23-1	LC-MS

3.5 Example for a LC/MS setting and parameters

3.5.1 LC/MS parameters and mass settings for PFOS

The selected LC/MS conditions differ slightly between laboratories and instruments. In Annex 2-D an example is listed from an accredited commercial laboratory. Mass ions (m/z) used for detection are listed in table 3-2 and for the described method in Annex 2-D.

4 Sampling screening and analysis of POP-PBDEs in articles, products and recycling streams

The production of POP-PBDE containing PBDE mixtures - commercial PentaBDE (c-PentaBDE) and commercial OctaBDE (c-OctaBDE) has stopped in 2004²⁶. Therefore, the specific issue of POP-PBDEs is their presence in articles in use and second-hand articles. Since POP-PBDEs are also present in certain recycling flows (WEEE plastic and polyurethane foam) products produced from these polymers from recycling can become POP-PBDE contaminated.

4.1 Products and articles possibly containing PBDE

A list of potentially POP-PBDE containing articles and materials are listed in Annex 1-B. If a study on the presence of POP-PBDE containing materials is planned this list can be assessed for possible relevant samples for the country.

4.2 Step by step approach for POP-PBDE monitoring in products and articles

To determine the occurrence and quantities of POP-PBDEs in different articles and materials including consumer products, representative samples can be purchased from retail outlets, from recycling plants (e.g. polymers from WEEE recycling plants) or other scrap (s).

Step 1: Survey of products and articles possibly containing POP-PBDEs

Before collecting samples, a survey can be conducted to preliminarily determine target presence of consumer products in use and in re-use that might contain POP-PBDE. Also some material flows known to possibly contain POP-PBDE and further used in recycling (e.g. plastic from WEEE recycling or polyurethane (PUR) foam from different end-of-life products) would be targeted considering the need to register for exemptions for POP-PBDE in recycling. Stakeholders for the different use groups might be contacted for support and input and possibly for providing samples. Relevant stakeholders to be contacted for the different use categories are listed in Annex 1-B.

Step 2: Sample collection

Samples can then be collected e.g. by the customs at the import or by competent authorities such as factory control or consumer protection authorities and related institutions (*Strengthening POPs Regulatory Framework Guidance*¹⁴). Sampling campaigns might also be conducted by research institutions possibly in collaboration with the ministry or other competent authorities or directly with the industry or waste management facilities.

Following criteria and information can be used by the stakeholders:

- a) The article or the material is listed in Annex 1-B and contains brominated flame retardants (e.g. the plastic of a computer is labelled as containing brominated flame retardants)
- b) The article or the material is listed in Annex 1-B and bromine is being detected by a screening method (see section 3.)

For the major POP-PBDE contaminated material flow WEEE plastic a detailed sampling methodology and a sampling protocol has been developed and is described in detail in [Wäger et al. \(2010\)](#)²⁷ in [Annex 1 and Annex 2](#). This sampling strategy and protocol can be applied (in a modified way) in other countries and regions having shredder plants for processing of WEEE.

An approach of sampling of single EEE for screening of POP-PBDE in e.g. Cathode Ray Tube casings of TV and PC is shortly described in Annex 4.

Step 3: Optional (further) screening in the laboratory

²⁶ With some uncertainty for possible production in China

²⁷ Wäger P, Schluep M, Müller E. (2010) RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. [Final Report](#) September 17, 2010.

Sample articles can be screened for the presence of bromine also in the laboratory where a more sensitive method might be available compared to the mobile equipments used in the field.

Rapid screening methods such as pyrolysis-GC/MS can be used for verifying the presence of PBDEs (and other BFRs types). Care has to be taken that by such methods without clean-up possibly present DecaBDE is not debrominated to POP-PBDEs, which would lead to false positive results.

When screening methods are applied it has to be ensured that the detection limit of the screening method is more sensitive than (below) the limit required for the screening (e.g. required from a certain legislation limit).

Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of PBDEs and have been reviewed. One accredited method used for commercial analysis is described in Annex 2-A. Further methods are described in the listed case studies below.

The extraction and clean-up of selected samples are described below.

4.3 Screening methods for bromine as indication for POP-PBDEs/BFRs

The screening of bromine can be a simple, rapid and cost-effective method for pre-selection steps of samples to determine which samples to select for the more complex and expensive confirmation analysis (see below).

A range of technologies are currently applied as screening tools for bromine in WEEE plastic in some recycling plants (see also PBDE BAT/BEP Guidelines⁴). These technologies can also be used for screening bromine in other materials like PUR foams, textile or rubber. Technologies used include Sliding Spark Spectroscopy, X-ray fluorescence (XRF), X-ray transmission (XRT) or Laser-Induced Breakdown Spectrometry (LIBS)²⁸.

Two of these technologies have been approved BFR screening capability in long time trials for separation of bromine containing polymers (WRAP 2006, Table 4-1)²⁹ and can be used for the screening of bromine in consumer goods in the field.

- X-ray fluorescence (XRF)
- Sliding spark spectroscopy

Other technologies capable for bromine screening but not practical for a simple screening approach, are for example:

- Neutron activation analysis
- X-ray transmission (XRT)

The technologies are shortly described below:

4.3.1 X-ray fluorescence (XRF) (table 4-1)

The X-ray fluorescence (XRF) technology can be used for detection of bromine in polymers and other materials with a detection limit for bromine of 10 to 100 ppm. XRF analysis is limited to the detection of bromine in the material, without any capacity to identify the type of BFR compound. Using handheld instruments the time requirement for a measurement is less than a minute. Precision of XRF screening measurements is limited and thus relative standard deviations of up to 30% may be obtained. However, this is only critical when measuring levels very close to a given threshold.

²⁸ Stepputat M, Noll R (2003) On-Line Detection of Heavy Metals and Brominated Flame Retardants in Technical Polymers with Laser-Induced Breakdown Spectrometry," Appl. Opt. 42, 6210-6220.

²⁹ WRAP (2006) Develop a process to separate brominated flame retardants from WEEE plastics Final Report Project code: PLA- 037 November 2006. Banbury, Waste Resources Action Program.

Care has to be taken with screening methods if the plastic is coated. Then the coatings need to be removed by scratching. Also dirt should be removed for an optimized screening. If a sample is heterogeneous (e.g. WEEE with different plastic parts) then the different parts need to be screened. XRF is a non-destructive method and can, therefore, be used to screen articles in stores or currently in use without damaging them.

XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. Whereas the primary radiation in bench top systems is generated from X-ray sources, handhelds work with beta emitters (^{63}Ni). As the sample is exposed to a beam of X-ray quanta from a tube, a proportion of these X-rays also reach the detector in the form of radiation **background** as a result of physical scattering processes including Rayleigh and Compton scattering. While the scattered Bremsstrahlung proportion generally produces a continuous background, the scattered characteristic radiation of the anode material contributes towards the **line spectrum**. Besides the lines of elements from the sample, the anode material's lines and the scattered Bremsstrahlung usually appear as well as a background. Background and characteristic scattering can be very effectively reduced by inserting a suitable absorption material between tube and sample.

The Bremsstrahlung and the characteristic radiation of the X-ray tube's anode material are used to excite the **characteristic radiation of the elements in the sample material**. Therefore, it is necessary to provide incident X-ray quanta, which are higher than the binding energy of the element's inner electrons.

When measuring X-rays, use is made of their ability to **ionize** atoms and molecules, i.e. to displace electrons from their bonds by energy transfer. In suitable detector materials, **pulses** of fluorescent X-rays with strengths proportional to the energy of the incident X-ray quanta, are produced by interaction of the incident X-rays and the analysed material. The information about the X-ray quanta's energy is contained in the registration of the pulse height. The number of X-ray quanta per unit of time, e.g. pulses per second (cps = counts per second, kcps = kilocounts per second), is called their **intensity** and contains in a first approximation the information about the concentration of the emitting elements in the sample.

The use of XRF instrument requires a specific instruction for the operator of handling such materials according to national guidelines. XRF with different X-ray source are available. Some of the XRF systems use a ^{63}Ni X-ray source and therefore a radioactive element. These equipments require special waste management at the end of the product's lifetime. Also non-radioactive instruments need careful operation and the personal using the equipment need to be trained for the specific equipment used.

Systems commercially available are e.g.:

- [Thermo Scientific Niton](#)
- [Olympus](#)
- [Bruker](#)
- Other providers

The use area of these XRF instruments is much broader than bromine and chlorine screening. Such instruments can e.g. be used for screening of heavy metals and other elements in consumer goods or contaminated soils. The cost of an instrument is approximately USD 30,000 to USD 50,000.

There are cheaper XRF equipments on the market with reduced functionality for e.g. specifically monitoring of RoHS compliance. These equipments can be used for screening of bromine and might be sufficient for this purpose.

4.3.2 Sliding spark spectroscopy (table 4-1)³⁰

Sliding spark spectroscopy is a surface screening method capable to rapidly detect bromine, chlorine, fluorine and inorganic additives at concentration down to approximately 0.1%. With a comparatively simple system, sliding spark spectroscopy allows direct in-situ analysis of handy, compact non-conductive material without prior sample preparation. Using handheld instruments the time requirement for a measurement lies within seconds.

Care has to be taken with screening methods if the plastic is coated. Then the coatings need to be removed by scratching. Also dirt should be removed for an optimized screening. If a sample is heterogeneous (e.g. WEEE with different plastic parts) then the different parts need to be screened.

Sliding Spark Spectroscopy is a destructive method in a sense that the measurement results in a burn spot from the spark. Therefore the articles to screen must be purchased.

The basic principle of the method is the thermal vaporization, ionization and excitation of a small amount of surface substrate using a train of high-current sliding sparks. The material components in the spark plasma are activated to emit radiation. From the atomic spectrum, information on the composition and the element concentration in the sample can be obtained.

Intense optical emission is observed when positionally stable high-current surface sparks (max. 800 Ampere/pulse) are sliding over compact non-conductive materials such as plastics, glasses, quartz filters or powder pellets. Substrate vaporization, ionization and excitation processes in the surface discharge plasma channel generate emission corresponding to neutral and ionic states. The spectra are essentially composed of lines emitted by the electrode material (e.g. copper and silver), from the substrate under investigation, radiation continuum as well as structured background from the surrounding air. Proper software treatment of the detected spectra allows the rapid multi-element screening of the investigated material. Thus, identification of bromine containing materials and inorganic additives (BFRs, fillers, stabilizers, BFR synergists) or chlorine containing plastics (PVC or chlorinated flame retardants), has been described (Schlummer and Mäurer 2006)³¹. The instrument costs approximately USD 6,000.

4.3.3 Neutron activation analysis

The neutron activation analysis (NAA) is a radiochemical multi-element analysis described as a “*supreme technique*” for elemental analysis. NAA is a sensitive multi-element analytical technique used for qualitative and quantitative analysis of major, minor, trace and rare elements. The method can be utilised for the determination of bromine content in plastic and was used for the Swiss market survey of BFR in products in 2004 and as validation method in the 2009 survey³². This technique can only be applied in laboratory. The instruments are rather expensive and of limited practicability as nuclear expertise is required.

4.3.4 X-ray transmission technology XRT

The XRT is non-mobile equipment applied in dismantling plants to sort scrap plastic by automatically monitoring the atomic density of materials. Therefore the instrument is not useful for screening for bromine in consumer goods.

³⁰ Seidel T, Golloch A, Beerwald H, Böhm G (1993) Sliding spark spectroscopy. *Fresenius' Journal of Analytical Chemistry* 347, 92-102.

³¹ Schlummer M, Maurer A (2006) Recycling of styrene polymers from shredded screen housings containing brominated flame retardants. *Journal of Applied Polymer Science* 102, 1262-1273.

³² Bantelmann E., Ammann A, Näf U, Trempe J (2010) Brominated flame retardants in products: Results of the Swiss market survey 2008 - pre-publication. *Proceedings of the 5th International Symposium on Brominated Flame Retardants*. April 7-9 2010, . Kyoto, Japan.

Table 4-1: Comparison of the hand held methods for screening of BFR containing plastic (WRAP 2006 with modifications).

Type:	X-Ray Fluorescence	Sliding Spark spectral analysis
Prime Function	Detect and quantify additives	Detect + quantify bromine and chlorine
Method of operation	Low power X-ray penetrates ~10mm into sample, detector measures distinct energy peaks from florescence of a range of elements to give ID and % concentration of additives	High voltage spark on surface creates plasma of vaporised material. Light spectra analysed for know peaks at Br and Cl wavelength to estimate % concentration
Weight approx	1.7 kg	0.75 kg (gun)
Portability	Excellent – battery powered, no cables	Reasonable – light to carry, but needs mains power.
Ruggedness	Excellent – built for on-site use in scrap-yards	Good – but care needed for fibre optic cable
Start-up speed	OK – 2-3 min's	Fast - < 1min
Operator manual	Good	Very good
Ergonomics	Easy – but careful to point away from user	Easy – but low flex cable to gun
Sample presentation & speed	Easy – hold gun on sample for 15 – 30 seconds	Very easy – 1 second to 'fire' spark
Read-out	OK – need to interpret ppm numbers on screen	Simple & clear
Adjustment	Not a problem	Easy to adjust base level reading to remove noise. Simple sensor cleaning method
Sample preparation	Thicker samples better (> 5 mm). Will detect surface contamination & coatings. Good for granular plastics	Clean surface required and flat area for good spark contact. Will detect dirt and coatings on surface
Accuracy	Very good – ppm levels of elements	Sufficient – to nearest 1% on Br/Cl concentration.
Repeatability	Excellent	Good – some noise around 0-1% level
Reliability	Very good	Very good
Speed	5-30 seconds	Fast – 1 second
User confidence	Good on primary elements, lower on chlorine.	High – except < 1% concentration level.
Price	Approx. USD 30000 - 50,000; cheaper if e.g. only RoHS elements are tested	Approx. USD 6,000
Operator skill level required	Technical operator to interpret results	Factory operator with basic training

4.3.5 Screening of Bromine by combustion-ion chromatography

IEC 62321-3-2 Ed.1 - Determination of certain substances in electrotechnical products has as Part 3-2 the "Screening of total bromine in electric and electronic products by combustion-ion chromatography (C-IC)". While this technology is not a mobile screening method it seems a reliable and useful method for the determination of bromine in polymers.

The IEC 62321-3-2 standard is in the drafting stage and an official version is expected in 2013.

4.4 Sample preparation, extraction and clean-up

Key matrices of PBDE in articles are (see POP-PBDE BAT/BEP Guidance):

- Flame retarded plastic of electronics (e.g. ABS, HIPS, PP)
- Flexible polyurethane foam (furniture, vehicle seating, mattresses), and rigid polyurethane foam (in construction)

Other materials with less use were textiles, rubber or drilling oils.

4.4.1 Preparation of plastic samples

The most relevant matrix for monitoring POP-PBDE in articles is plastic samples with 90% of c-OctaBDE used in ABS.

Preparation of single polymer samples

In case of analysis of single polymer item (plastic from a computer, TV set or plastic toy) no further pre-treatment of the plastic is necessary, if for the extraction the below described dissolution/precipitation approach is chosen.

For other extraction methods single items have to be ground by a suitable mill, preferably using liquid nitrogen. Grinding methods could be evaluated for debromination of PBDE/BFRs and the formation potential of polybrominated dibenzofurans (PBDFs) from PBDE.

Preparation of mixed polymer samples

In case the average PBDE/BFR content of a mixed WEEE plastics needs to be determined and a careful grinding and homogenisation processes is required to gain a laboratory sample suitable to reflect a bulk sample of several kg to tonnes. This process has to be performed stepwise (50 kg out of a tonne, 1 kg out of 50 kg, 50 g out of 1 kg, 1 g out of 50 g). With decreasing sample size, decreasing particle sizes are recommended, ending up with < 500 µm for the final sample.

Each grinding step should be performed with suitable mills and sieve sizes. The final particle size < 500 µm is recommended for the subsequent solid liquid extraction. The smaller the particle size the more effective is the extraction, especially when polar extraction solvents are chosen, which do not dissolve for example polystyrene based polymers that are frequently a major share in WEEE plastic fractions.

4.4.2 Extraction of POP-PBDE and other BFRs from polymers

A reliable analysis of PBDE/BFRs in polymers necessitates an efficient sample extraction process of the additives from the matrix. Extraction is the term given to the process of isolating specific compounds from a bulk matrix. For the determination of additive BFRs in polymeric materials, solvent extraction plays an important role in the overall procedure.

There are two main approaches for extracting PBDE/BFRs from polymers: A) solid-liquid extraction and B) dissolution/precipitation. The solid-liquid approach extracts PBDE and BFR from ground solid plastics and is applicable, when there is no or only a minor dissolution of solvent and polymer, since partly dissolved polymers contaminate the GC-MS system (if not completely removed in the clean-up).

The dissolution/precipitation approach dissolves both, polymeric matrix and POP-PBDE/BFR and the dissolved polymer is removed in a second precipitation step (see below). Dissolution of plastics is described in further detail in Braun (1999).³³

Since there is no unique solvent to dissolve all polymers in WEEE plastics, the solid-liquid approach is favourable for mixed WEEE plastic fractions, whereas the latter is suitable for polystyrene based

³³ Dietrich Braun, Simple methods for identification of plastics, 4th ed., 1999, Carl Hanser Verlag, München, Germany.

WEEE fractions (a major fraction of WEEE plastics) or analysis of single housings of a specific electronic equipment.

Solid-liquid extraction

Solid liquid extraction is the most commonly used method in trace analysis. The compounds of interest are isolated using a range of procedures, such as vigorous shaking, ultrasonication, Soxhlet extraction and microwave-assisted or pressurized liquid extraction (PLE, e.g. accelerated solvent extraction). Note, that light and elevated temperatures created during ultrasonication, microwave-assisted extraction or PLE might cause unintended PBDE/BFR degradation.

Best recoveries are obtained by Soxhlet extraction applying solvent mixtures like methanol or 1-Propanol with up to 25% of a non polar solvent like toluene. The extraction time depends on the applied Soxhlet apparatus, but should allow for at least 30 extraction cycles. The Soxhlet extraction is also recommended for other matrices not discussed here (PUR foam, textiles and rubber) with appropriate grinding.

Alternatively PLE with isooctane can be employed in the analysis of PBDE/BFR for WEEE plastic, other plastic items or polyurethane foams. At 100°C three static extraction cycles of 45 minutes each are recommended. However, if there is a considerable amount of polyolefins in the respective WEEE fraction, addition of at least 20% of alcohol (e.g. 1-Propanol) to the extract is required.

Extraction of PBDE/BFR by “Dissolution and Precipitation” method

One effective approach for extraction of PBDE/BFRs from the polymer is the complete dissolution of the polymer in an appropriate solvent. Selecting a solvent capable of dissolving the polymer at room temperature is most desirable, since elevated temperatures may result in thermal stress that might cause PBDE/BFR degradation. This approach yields good recovery efficiency for the respective BFR. For some polymer types (e.g. polyurethane), however, suitable solvating solvents are not available. Chromatography issues related to system entrapment of the resin and other matrix compounds may also be problematic following a complete polymer dissolution approach. Such entrapment can result in poor chromatographic resolution, hindering the correct detection and identification of compounds and necessitating increased maintenance of the GC-MS system. Adding a second “non-solvent” to the extract to precipitate the interfering components (e.g. resin) can be a useful additional step. Ideally, the polymer and other interfering additives (plasticizers, dye stuffs, etc.) are precipitated and the target analytes remain quantitatively in the extract. This method can, however, also generate analyte losses either via target analyte adsorption in the precipitate, or if the solubility of the target analyte is affected negatively by the non-solvent. Pöhlein and co-workers (2005) also developed two methods to identify and quantify BFRs in styrenic polymers.

Extraction procedure of key plastics formerly treated with POP-PBDE

The extraction of POP-PBDEs and other brominated flame retardants from the polymer (ABS, PS, PVC, ABS/PC blend, PPE/PS blends) is performed by dissolution with tetrahydrofuran and precipitation is done with either ethanol (Schlummer et al. 2006)³⁴, 1-propanol (Schlummer et al. 2007)³⁵ or *n*-heptane. This approach yields high extraction efficiency and short extraction time.

The extraction steps for ABS, PS, PVC, ABS/PC blend, PPE/PS blends are given below;

- 0.5 grams of the plastic samples are weighed into a well-labelled extraction glass vial covered with alumina foil paper. Dark-brown glass vial are recommendable.

³⁴ Schlummer M, Mäurer A, Leitner T, Spruzina W (2006) Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE). Waste Management Research 24, 573-583.

³⁵ Schlummer M, Gruber L, Mäurer A, Wolz G, van Eldik R (2007) Characterisation of polymer fractions from waste electrical and electronic equipment (WEEE) and implications for waste management. Chemosphere 67, 1866-1876.

- 5 ml of tetrahydrofuran (THF) is added.
- The glass vial is tightly capped and placed on a shaker for two hours.
- After complete dissolution of the polymer sample, 6 – 12 ml of *n*-heptane is added stepwise with rigorous shaking until a good precipitate is formed.
- The glass vial is capped and placed on the shaker for 15 minutes until a clear solution is obtained.
- The glass vial is then allowed to stand for another 15 minutes.
- The extract is then decanted into a well-labelled, pre-weighed collection glass vial covered with alumina foil paper.
- The precipitate is re-dissolved in 5 ml THF and placed on the shaker for 15 minutes.
- Another 6 – 12 ml of *n*-heptane is added stepwise with rigorous shaking and the vial is placed on the shaker for 15 minutes.
- The extract is decanted into the glass vial.
- The entire procedure is repeated thrice.
- The weight of the extract is calculated from the difference between weight of glass vial plus extract and the weight of the bottle.
- The residual polymer is removed from the glass vial and kept in foil paper.

Extraction procedure for polypropylene samples:

- 0.5 gram of the polymer sample is weighed into a well-labelled extraction glass vial.
- 30 grams of xylene solution is added.
- The glass vial is loosely corked and place on the heating mantle for 1 hour at a temperature of 105 °C with a magnetic stirrer.
- After complete dissolution of the polymer sample, the glass vial is removed and allowed to cool to room temperature.
- 10 ml of acetone is added step wisely with little shaking until a gel-like precipitate is formed.
- The extract is then filtered using paper filter into a well-labelled, pre-weighed glass vial covered with alumina foil paper.
- The weight of the extract is calculated from the difference between weight of glass vial plus extract and the weight of the bottle.
- The residual polymer is removed from the filter paper and kept in foil paper.

Dissolution of other types of plastics is described in Braun (1999)³⁶.

Clean-up of the plastic extracts

The easiest clean-up step consists of a filtration through a 0.45 µm filter disk (PTFE membrane) and the cleaned sample is placed in GC vials prior to chromatographic analysis. However, this approach removes only polymers and oligomers, which may have precipitated upon storage of extracts at lower temperatures.

Considerably better cleaning efficiencies can be reached by column chromatography. For non-polar extracts (isooctane), a Silica SPE column may be used (100-1000 mg) after pre-wash with *n*-heptane.

³⁶ Braun D (1999) Simple methods for identification of plastics, 4th ed. 1999, Carl Hanser Verlag, München, Germany-

The sample extracts is loaded on top of the SPE and the collection of target POP-PBDE starts directly with the sample loading. To complete the elution of the analytes another 10 ml n-heptane are added on top and collected after SPE passage.

If the analysis only targets POP BDE, a sulfuric acid treatment is recommended. For this clean-up step a glass column with a diameter of 10 mm is filled with 1 g of neutral silica and 5 to 10 g of H₂SO₄ impregnated silica (44% by weight). The column is pre-washed with 30 ml of n-heptane, before the sample extract is loaded. The collection of target POP-PBDE fraction starts directly with the sample loading. To complete the elution of the analytes, another 100 ml n-heptane are added on top and collected after passage of the column.

Before GC-MS analysis, the volumes of cleaned extracts are reduced to about 1-100 ml (depending on the expected concentrations in the sample) using a rotary evaporator.

4.4.3 Extraction of flexible and rigid polyurethane foam (Bergmann 2006)³⁷

For extraction of POP-PBDE from polyurethane, solid-liquid extraction is sufficient to achieve an excellent recovery of POP-PBDE. Soxhlet extraction with toluene was found most effective. After 2 hours extraction time, exhaustive extraction is achieved without detection of PBDE in extracted PUR foam.

4.4.4 Specific considerations on quality assurance

Common procedures for the quality assurance of analysis of newly listed POP are described in section 2 above. Specific measures for POP-PBDEs (and other BFRs) include:

- measures to minimise exposure of samples to UV-light to avoid losses through degradation
- all glass vials either covered with alumina foil paper or use of brown glassware
- lamps in the laboratory to cover with UV-protective film

4.5 Quantitative (and semi-quantitative) analysis

4.5.1 POP-PBDE relevant to the Stockholm Convention and measurement standards

A measurement method for PBDE for Stockholm Convention purposes need to cover the tetraBDEs, pentaBDEs, hexaBDEs and heptaBDEs (major congeners of commercial mixtures are listed in Annex 3). The higher brominated homologues (octaBDE, nonaBDE and decaBDE) are not considered POP-PBDEs but might be analysed together with POP-PBDE.

POP-PBDE standard

For the quantification of POP-PBDE in articles normally external standardization is used. In the standard approach of Fraunhofer Institute working on recycling of WEEE polymers since a decade (Schlummer et al. 2006)³⁸ following PBDE and BFR standards are used for monitoring of POP-PBDEs and other relevant BFRs³⁹: major c-OctaBDE congeners (see Figure 4-1), decaBDE, 3,3',5,5'-

³⁷ Meike Bergmann (2006) Bestimmung polybromierter Diphenylether in Kunststoffen und Untersuchungen zum Emissionsverhalten. PhD, Technical University Berlin.

³⁸ Schlummer M, Maurer A, Leitner T, Spruzina W (2006) Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE). Waste Management Research 24, 573-583.

³⁹ Major flame retardants should be included in the standard to ensure that BFRs are separated from POP-PBDEs especially when ECD detector is used. Also for the recycling of polymers it is important to know what BFR restricted by RoHS regulation are present. Therefore major BFRs used in EEE polymers are included.

tetrabromobisphenol A (TBBPA) and tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPE). At least these standards are recommended since depending on the column those major used BFRs can co-elute with POP-PBDEs and therefore need to be considered. These main BFR could also be evaluated (possibly determined) to be able to describe the correct peaks in particular when using ECD detectors used preferably in developing countries. The BFRs standard solution are also used to check the chromatographic separation and that other major BFRs do not co-elute with POP-PBDE (relevant in particular when using ECD technique). In Figure 4-1 the chromatograms of WEEE plastics are shown containing mixtures of flame retardants including POP-PBDEs. On the column used the TBBPA co-elutes with POP-PBDE 153.

The standards are stored under exclusion of lights to prevent photolytic transformation. Stock solutions of individual standard are prepared by weighing and dissolving the crystalline solids into THF. The concentration of each BFRs standard is approximately 1000 ppm. Working solutions are prepared directly before use by diluting the standard to 5 concentrations between 1 and 100 ppm. A mixture of BFR standards is dissolved together in appropriate portion of THF and *n*-heptane. For Stockholm Convention purposes also another calibration range might have to be used if a different 'low POPs' limit would be established from the 0.1% limit used for RoHS⁴⁰.

4.5.2 Instrumental analysis of POP-PBDEs

Separation techniques

The state-of-the-art analytical technique for analysis of the POP-PBDE congeners addressed by the Stockholm Convention (tetraBDE to heptaBDE) are chromatographic techniques^{41, 42}.

As chromatographic technique gas chromatography (GC) is normally used. Liquid chromatography (LC, HPLC) has rarely been applied, particularly because of the lower separation efficiency. The international standard IEC 62321 describes in addition to GC/MS also a High Performance Liquid Chromatography method coupled to Ultra Violet detection (HPLC/UV). GC separation is normally performed on a non-polar 10-30 meter GC column⁴³. Injection temperature should be below 260°C or cold on-column injection should be applied, since higher temperature might lead to a degradation of DecaBDE and possibly lead to lower brominated PBDE artefacts.

Detectors: Mass spectrometer, Electron Capture Detector

Different detection technologies can be used for PBDEs/BFRs analysis. State of the art detection is mass spectrometry. Electron Capture Detector (ECD) is also suitable for analysing POP-PBDE and has for the monitoring of PBDE in articles and products the advantage of a higher robustness and simpler cleaning of the detector (table 4-2). The advantages and drawbacks of the main utilized detection techniques are described in the table 4-2:

As mentioned for the separation unit, it is also important that the detector temperatures are not too low (<300°C) in order to avoid sinks for DecaBDE but also not too high (>340°C) in order to avoid degradation. In conclusion, 330-340°C is recommended for ECD detector temperatures, and 320-330

⁴⁰ The 0.1% RoHS limit is not based on risk considerations and is 20 times higher than the current provisional 'low POPs' limit for POP pesticides and PCBs.

⁴¹ Covaci A, Voorspoels S, de Boer J (2003) Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers in environmental and human samples - a review. *Environ Int* 29, 735-756.

⁴² International Electrotechnical Commission (2008). International Standard IEC 62321 Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers). Edition 1.0 2008-12 (also adopted as EN 62321:2009), IEC Technical committee TC 111.

⁴³ If also DecaBDE is to be monitored, a shorter column (preferably 15 meter) are normally used.

for the detector side of the column. MS ion source temperatures however, are usually set below 280°C in order to increase the life time of the filaments.

PBDE detection with mass spectrometry

Sensitive EI-MS analysis is performed in single ion reaction mode (e.g. single ion monitoring SIM mode), monitoring the 2 to 3 most abundant isotope clusters of the precursor (molecular) ions (for triBDE to pentaBDE) and the 2 to 3 most abundant M-2 Br isotope clusters for (HexaBDE to DecaBDE). Normally at least 2-3 SIM windows are defined, sometimes SIM windows for each kind of homologues are built-up (see Annex 2-1).

For analysis of PBDE/BFR polymers low resolution mass spectrometry (LRMS)⁴⁴ is sensitive enough. Modern GC-EI-LRMS instruments are sensitive enough in the scan mode and can be run with a scan from 400-1000 m/z.

Electron capture negative ionisation (ECNI) coupled to LRMS has been reported to provide better sensitivities for higher brominated PBDE ECNI produces mainly $m/z=79/81$ (bromine isotopes), which is monitored in one window. The disadvantage of this technique is that the compounds peaks do no longer provide mass spectral information and peaks are allocated by retention times only (as for ECD). The second disadvantage is, that ¹³C-labelled internal standards cannot be applied due to the same retention time and masses used. ECNI has also the disadvantage that the ionization is highly dependent on the bromine substitution pattern, making quantification inaccurate when ¹³C-labelled internal standards cannot be used for each individual analyte.

Table 4-2: Advantages and drawbacks of different detection techniques for PBDE/BFRs are highlighted in the table (Covaci et al., 2003 and 2007)⁴⁵

Detection	Advantages	Drawbacks
ECD	purchase cost maintenance cost ease of use	fair sensitivity for BFRs instability of linear range very low selectivity
EI-LRMS	facilitates the use of labelled standards good selectivity	low sensitivity
ECNI-LRMS	good sensitivity good selectivity for brominated compounds	frequent source maintenance required
EI-HRMS	good sensitivity very good selectivity	purchase cost maintenance cost difficult to use higher "down-time"

PBDE analysis with Electron Capture Detector (ECD)

Electron Capture Detector (ECD) is an appropriate detector for brominated aromatic compounds. The advantage of the detector is the robustness, the relative low costs and the ease of

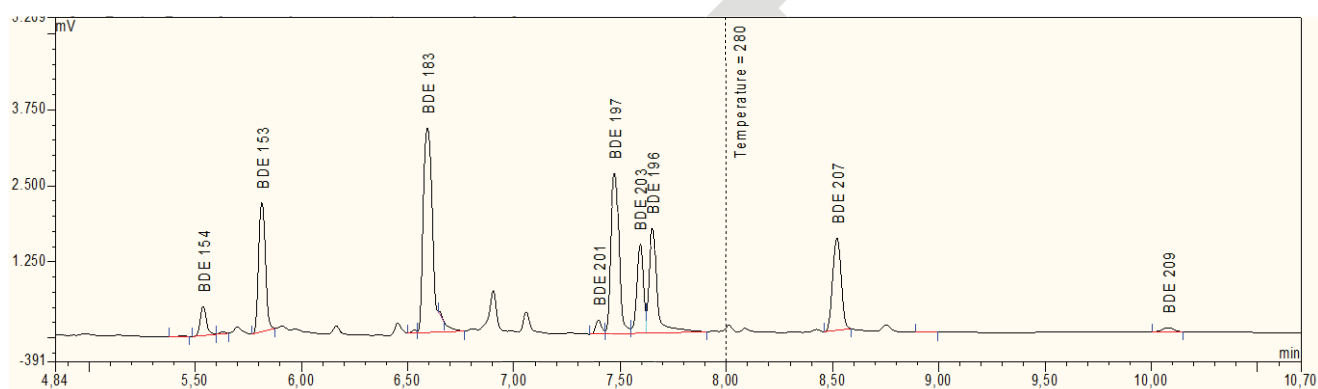
⁴⁴ The more sensitive and expensive HRMS requires highly trained and experienced lab personnel is not needed for this matrix.

⁴⁵ Covaci A, Voorspoels S, Ramos L, Neels H, Blust R (2007) Recent developments in the analysis of brominated flame retardants and brominated natural compounds. Journal of Chromatography A 1153, 145-171.

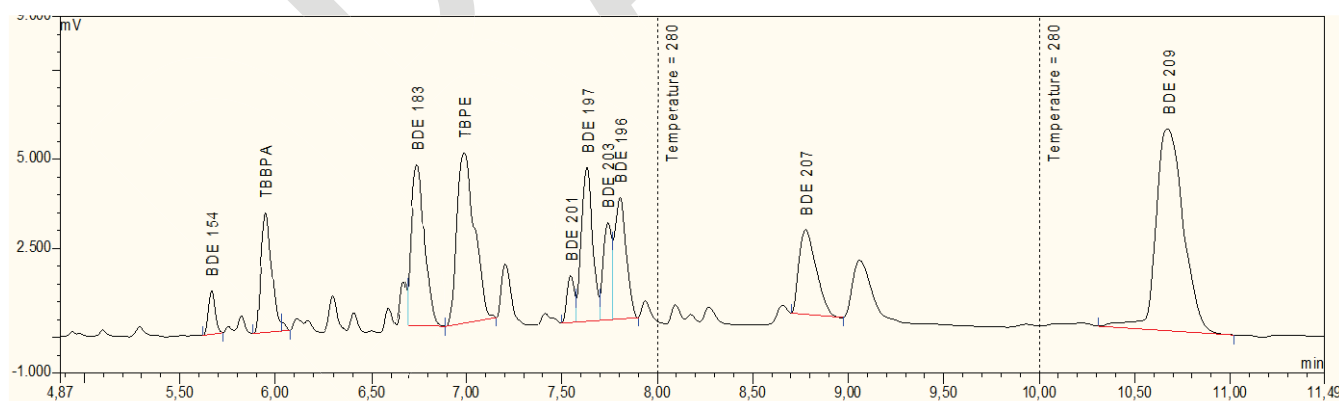
use (see table 2). The robustness of the detector and the slightly higher operation temperature is a particular advantage of the ECD detector when analysing “dirty” samples like polymers having often oligomers in the extracts.

However, since the peak in the ECD does not include structural information, only the retention time is used to determine the respective compound. Since PBDEs are present as mixtures in the polymers they have a specific fingerprint which can be used for confirmation. An interlaboratory comparison study revealed a good agreement of GC-ECD and various GC-MS techniques (Zeleny et al. 2010)⁴⁶.

The recognition and interpretation of chromatograms from ECD detector need some experience to determine POP-PBDE in particular if BFR mixtures are present in recycled plastics (see examples in Figure 4-1 below). This might be more critical in future since the number of brominated flame retardants are increasing (according to the bromine industry there are approximately 75 BFRs on the market). In addition other heteroatoms with good electron capturing abilities, such as the chlorinated and fluorinated organic compounds can give high ECD response, which can interfere with the analysis and give false positives.

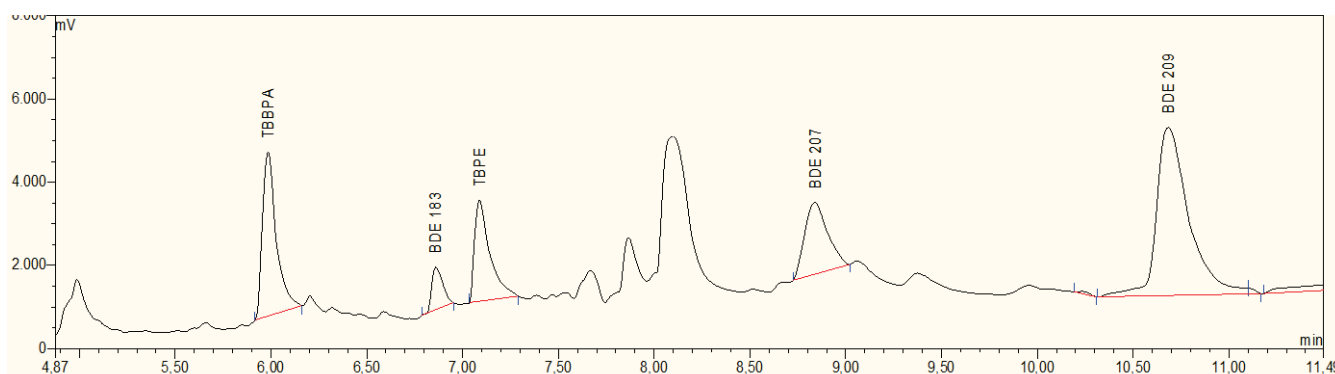


a) GC ECD chromatogram of standard solution of commercial-OctaBDE (5µg/ml)



b) GC-ECD chromatogram of a sample containing different BFRs including commercial-OctaBDE as a major BFR (Please note: TBBPA co-elutes on this column with BDE 153)

⁴⁶ Zeleny R, Voorspoels S et al. (2010) Evaluation of the state-of-the-art measurement capabilities for selected PBDE and decaBB in plastic by the international intercomparison CCQM-P114. *Analytical and Bioanalytical Chemistry* 396, 1501-1511.



c) Sample containing different technical BFR including traces of technical OctaBDE

Figure 4-1: GC/ECD chromatograms of a) c-OctaBDE standard compared to two extracts from WEEE plastic (b) and c) with BFR mixtures including c-OctaBDE and other BFRs (GC separation was obtained with a Phenomenex Zebron™ ZB-5HT Inferno™ (15 m x 0.25 mm x 0.1 µm), temperature program: 140°C (1 min), 20 °C/min (280°C), 4 °C/min (300°C), 20 °C/min (320°C, 5 min)

4.5.3 Example of a GC/MS setting and parameters for POP-PBDEs (and HBB)

The selected GC/MS conditions differ slightly between laboratories. Also different GC columns can be used. In Annex 2-A an example of GC/MS condition for the analysis of PBDE are given along with the related chromatogram (Annex 2-A). Also the correct masses for the MS setting are listed.

4.5.4 International and national standards for PBDE analysis

International Standard for determination of regulated substances in electronics (IEC 62321)

An International Standard IEC 62321 ed.1⁴⁷ has been developed for “Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)” and the second edition is currently under development. The method describes details on sample preparation and analysis.

The Determination of PBDE (monoBDE to decaBDE) and PBB (monoBB to decaBB) in polymers by GC-MS is described in Annex A of IEC 62321 - including extraction, analysis and quality assurance. The method has especially been optimized for the concentration range of 100 mg/kg and 1000 mg/kg due to the requirements of EU RoHS Directive compliance.

A working group (IEC TC111 WG 3) is currently drafting the 2nd edition of the international standard (IS 62321; 2nd edition) with determination of PBDE and PBB as Part 6. Publication of this version is expected in 2013.

⁴⁷ International Electrotechnical Commission (2008). International Standard IEC 62321 Electrotechnical products -Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers). Edition 1.0 2008-12 (also adopted as EN 62321:2009), IEC Technical committee TC 111.

German national standard for determination of PentaBDE and OctaBDE in plastic materials in respect to the RoHS directive (Kemmlein et al. 2005)⁴⁸

A standard method for determination of PentaBDE and OctaBDE in plastic materials in respect to the RoHS directive (Directive 2003/11/EC, Directive 76/769/EEC) has been developed on behalf of the German Environmental Agency (Kemmlein et al. 2005). The method includes extraction, clean-up and measurement procedures. The study has also validated the method for different polymers and assessed for reproducibility and repeatability. The compounds analysed in this method are however limited to certain PentaBDE (BDE85 (2,2',3,4,4'-pentaBDE), BDE99 (2,2',4,4',5-pentaBDE), BDE100 (2,2',4,4',6-pentaBDE)) and OctaBDE (BDE203 (2,2',3,4,4',5,5',6-octaBDE), BDE196 (2,2',3,3',4,4',5,6'-octaBDE), BDE197 (2,2',3,3',4,4',6,6'-OctaBDE)) since the current RoHS limit is defined for Σ PentaBDE and Σ OctaBDE with a limit of 0.1% each.

US EPA method 1614⁴⁹ for PBDE in water, soil, sediments and tissue

The US Environmental Protection Agency (USEPA) has developed a standard for the analysis of polybrominated diphenyl ethers in water soil, sediment and tissue by HRGC/HRMS.

The GC/MS analysis described in this standard available on the internet can also be used for the analysis of POP-PBDE from articles and products after appropriate clean-up. One important consideration is the concentration range defined in the method. This range needs possibly to be adjusted by dilution of the sample.

4.5.5 Rapid determination techniques for PBDE analysis with minimised clean-up

For more rapid analysis (compared to the standard GC methods with clean-up) some techniques have been developed for faster (but less effective) extraction techniques and to omit the clean-up steps. Pöhlein et al. (2008)⁵⁰ developed a rapid screening method for BFR including PBB and PBDE in polymer samples using ultra sonic extraction and GC-MS analysis.

An alternative method to screen brominated flame retardants including PBDE in a selective mode without extraction and clean-up has been established. Danzer et al. (1997)⁵¹ used online pyrolysis of pulverised plastic and analysed samples with gas chromatography coupled to mass spectroscopic detection (py-GC/MS).

A thermo-desorption method for polymers was developed for rapid screening of polymers of 100 TV sets and 80 computers (Rieß et al. 2000)⁵². The pyrolysis GC/MS method has since been developed to a commercially available application by Shimadzu with a 48 sample auto-sampler (Shimadzu 2010)⁵³.

An independent evaluation of the quality of results of such rapid screenings has not been performed yet. The pyrolysis of matrices might lead to some degradation of PBDE including debromination reactions which have been reported for GC/MS analysis.

⁴⁸ Kemmlein, S., Bergmann, M, Jann, O (2005) Standard measurement method for the determination of polybrominated flame retardants (pentabromo diphenylether, octabromo diphenylether) in products Nr. 31/2005 UBAFBNr 000839/e.Förderkennzeichen 202 67 300, Umweltbundesamt.

⁴⁹ US EPA method 1614

http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_09_11_methods_method_1614.pdf

⁵⁰ Pöhlein M, Bertran RU, Wolf M, van Eldik R (2008) Versatile and fast gas chromatographic determination of frequently used brominated flame retardants in styrenic polymers. J. of Chromatography A 1203, 217-228.

⁵¹ Danzer B, Riess M, Thoma H, Vierle O, van Eldik R (1997) Pyrolysis of Plastics Containing Brominated Flame Retardants. Organohalogen Compounds 31, 108-113

⁵² Rieß M, Ernst T, Popp R, Müller B, Thoma H, Vierle O, Wolf M, van Eldik R (2000) Analysis of flame retarded polymers and recycling materials. Chemosphere 40, 937-941.

⁵³ Shimadzu (2010). Pyrolysis GC/MS of Brominated Flame retardants

http://www2.shimadzu.com/applications/gcms/Appl_GCMS_PBDE_07C_070_en.pdf

Such rapid analytical techniques with reduced (or no) clean-up steps reduces the number of injections between GC/MS (or other instrument) maintenance and shortens the lifetime of the GC columns (even if pre-columns are used). Both possible drawbacks need to be assessed if such rapid analysis might be used as options for POP-PBDE screenings.

4.5.6 Commercial availability of PBDE analysis

Standard commercial GC/MS analysis of PBDE in plastic and other materials is widely available in industrial countries. This is largely because of the requirement of RoHS compliance. The Commercial GC/MS analysis of brominated flame retardants are, however, still relatively expensive. The Price in Europe for PBDE analysis starts from approximately 130 EURO per sample⁵⁴.

⁵⁴ This can be compared to PCB analysis in transformer oil which is currently available with GC/MS for approx. EURO 50 per sample. Much of this cost difference can be explained by the more complex and time consuming extraction and clean-up of the polymer matrix required for PBDE analysis compared to a PCB oil.

5 Sampling and analysis of Chlordane in products and articles

The production and use of chlordane has stopped 1991 and a recent survey for chlordane on the pesticide market did not find any indication of current trade.

However, food export from chlordane contaminated areas (Guadeloupe, Martinique) might be relevant and could be monitored.

5.1 Products and articles possibly containing chlordane

5.1.1 Food products

Since chlordane has generated large contaminated sites in areas where it has been applied (e.g. Martinique and Guadeloupe) specific food products in these areas might be contaminated (e.g. fish or shrimp) as revealed by monitoring (Garrigues 2011)⁵⁵. If such potentially chlordane contaminated food is on the local market or exported then chlordane residue levels would be analysed.

5.1.2 Unintentional trace contaminants in chemicals produced from hexachlorocyclopentadiene

The formation of chlordane involves the dimerization of hexachlorocyclopentadiene. Therefore other dimerization products of hexachlorocyclopentadiene might contain chlordane as unintentionally trace compounds. Therefore products produced from hexachlorocyclopentadiene could be monitored for chlordane and other POPs produced from hexachlorocyclopentadiene dimerization (e.g. aldrin, dieldrin, endrin, mirex, endosulfan).

5.2 Analysis of Chlordane

Chlordane seems unstable under GC conditions⁵⁶ and need therefore be analysed by liquid chromatography. A methodology used by an experienced laboratory is described in Annex 2-E.

⁵⁵ Garrigues P. Chlordane in the French West Indies: Overview of research activities dealing with soil and aquatic ecosystems. Presentation at RECETOX workshop on "Research needs 10 years Stockholm Convention" 22-24 May 2011 Brno/Czech Republic. <http://www.recetox.muni.cz/res/file/pdf/workshop/BrnoPG1-2.pdf>

⁵⁶ Malisch R, WHO POPs reference laboratory, personal communication with Roland Weber 22.02.2012.

6 Sampling and analysis of PeCBz/HCB and other unintentionally produced POPs in products and articles

Unintentionally produced PeCBz and HCB are formed in parallel to PCDD/PCDF and therefore are present in the same processes and products as PCDD/PCDF (see [UNEP Toolkit](#); Weber et al. 2008, [Takasuga et al. 2009](#)⁵⁷). HCB and PeCBz are formed in some chemical productions in particular high concentrations including certain pigments ([Government of Japan 2006](#)⁵⁸ and [2007](#)⁵⁹) or production of major organochlorine solvents (Jacoff et al. 1986⁶⁰; [Weber et al. 2011](#)⁶¹). The ratio of PeCBz to HCB depends on the level of chlorination. In productions of perchlorinated compounds (e.g. tetrachloroethene), HCB might be present in considerable higher concentration compared to PeCBz. In other processes of only partly chlorinated organic compounds (trichloroethene, dichloroethane) the PeCBz might be present in concentration comparable or possibly even higher compared to HCB. Systematic studies on such basic relationships of HCB, PeCBz and other unintentionally POPs are missing up to now. Depending on the purification process of these chemicals PeCBz and HCB (and other unintentionally POPs) remain as production residues (e.g. heavy distillates) or are transferred into the product.

6.1 Products and articles possibly containing PeCBz/HCB

Articles and products (chemicals and chemical mixtures) possibly containing PeCBz, HCB or other unintentionally produced POPs are listed in Annex 1-3. Furthermore all organochlorine chemicals might be suspected to contain unintentionally produced POPs at some level.

6.2 Extraction of articles/products possibly containing PeCBz/HCB and clean-up

For the range of chemicals and some articles and products that dissolve in solvents, specific extraction procedures are not required. For those chemicals and articles which do not dissolve readily in solvents, the chosen extraction process needs to have proven high or exhaustive extraction of the unintentionally POPs from the articles and products.

6.2.1 Analysis of solvents

The solvent is directly spiked (with ¹³C₆-HCB and ¹³C₆-PeCBz), the volume is reduced by rotary evaporator and injected without clean-up. For solvents with larger impurities a clean-up with alumina column might be performed.

⁵⁷ Takasuga T, Takemori H, Yamamoto T, Higashino K, Sasaki Y, Weber R. (2009) The fingerprint of chlorinated aromatic compounds in contaminated sites from chloralkali process and a historic chlorine production using GC-HR-TOF-MS screening. [Organohalogen Compounds 71, 2239-2244](#).

⁵⁸ Government of Japan (2006) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in TCPA and Solvent Red 135. November 2006.

⁵⁹ Government of Japan (2007) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in Other Pigments Derived from TCPA and Phthalocyanine

⁶⁰ Jacoff F, Scarberry R, Rosa D (1986) Source assessment of hexachlorobenzene from the organic chemical manufacturing industry, in Morris, C.R.; Cabral, J.R.P. Hexachlorobenzene: Proceedings of an International Symposium; pp. 31-37.

⁶¹ Weber R, Watson A, Malkov M, Costner P, Vijgen J (2011) Unintentionally produced hexachlorobenzene and pentachlorobenzene POPs waste from solvent production – the need to establish emission factors and inventories. [Organohalogen Compounds 73, 2205-2208](#).

6.2.2 Extraction and analysis of chemicals dissolving in solvent

Most organochlorine chemicals will dissolve in solvents such as dichloromethane, toluene or n-heptane⁶². A test of dissolution of a few milligrams in a few ml solvent can be done (e.g. in a 5 ml sample vial) possibly assisted by ultrasonic treatment.

Some pesticides might contain inorganic materials in the formulation, which will not dissolve. However the organic fraction is normally dissolved in particular when the inorganic matrix is just an additive in the pesticide formulation. However in some cases the organic trace contaminants are partly incorporated in the inorganic matrix as in the case of pigments or certain ashes. In these cases the inorganic matrix has to be broken up by appropriate pre-treatment (see below).

6.2.3 Extraction of pigments and other samples where matrix need to be broken up

The structure of pigments need to be dissolved, so that unintentional POPs possibly included in the pigment layers can be sufficiently extracted. For this first step pigments are treated with sulphuric acid. 0.01 g of a pigment sample is spiked (with ¹³C₆-HCB and ¹³C₆-PeCBz or other unintentional POPs standards) and dissolved in sulphuric acid for a constant volume of 50 ml and a clean-up spike added.

The dissolved pigment solution is extracted three times with n-heptane. The n-heptane is concentrated to approx. 1 ml for the cleanup.

6.2.4 Clean-up

Different clean-up procedures are used depending on the levels, which needed to be detected for the different unintentional POPs (e.g. for HCB/PeCBz detection in the high ppb range might be sufficient while for PCDD/PCDF ppt level needs to be detected). Extraction and clean-up procedures are described e.g. in respective publications/report that have analysed unintentionally POPs in pigments or pesticides (see references for case studies below such as Holt et al. 2010; [Government of Japan 2006](#) and [2007](#); Liu et al. 2012).

6.3 Quantitative instrumental analysis

For PeCBz and HCB the measurement can be performed with low resolution MS or ECD. Conditions for GC/MS are described in Annex 2-C.

For the PCDD/PCDF analysis different international standards have been developed (e.g. EN 1948-3; [USEPA Method 8290A](#)⁶³).

⁶² The use of heptane is preferred compared to hexane (neurotoxic; should be substituted were feasible).

⁶³ [US EPA method 8290A](#)

ANNEX 1 Articles/products which might contain POPs listed in 2009 and 2011

Annex 1–A PFOS and PFOS related chemicals in articles and products

PFOS and related chemicals in production and as products

PFOS and related chemicals are currently produced in at least three countries (China, Germany, and Italy). Some trade names and product names are available and have been listed in an Annex of the “POPs Customs Control Guidance”⁶⁴.

PFOS in fire-fighting foams

Specific fire-fighting foams (aqueous film forming foams (AFFF)) with PFOS or other PFCs are used for extinguishing liquid fuel fires. They are especially used at installations and plants where large quantities of flammable liquids are stored. PFOS containing fire fighting foams are still on the market.

Fire fighting foam is listed as an acceptable purpose. Therefore, countries can register for this use, which has to be considered then for monitoring. Fire fighting foams can be sampled at import from customs. Additionally stocks on the fire-fighting services level would be sampled and analysed. Box A-1 list fire fighting services and locations with a high probability of AFFF use which could be inspected and where samples could be taken. However, fire-fighting services from the city/region also might have AFFF for specific uses and these would be assessed.

Box A-1: Fire-fighting services and locations where AFFF foams are mainly used

- fire-fighting training sites
- airports
- oil refineries
- military areas
- offshore installations, mobile rigs
- onshore gas terminals, onshore installations for gas and oil extraction
- storage facilities at industrial sites
- tank farms
- waste management installations
- hospitals
- car parks
- ships and ferries

⁶⁴ Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft).

Metal plating industries

PFOS related chemicals are mainly used as surfactant/wetting agent/mist suppressants in hard and decorative chrome plating, which can reduce the emission of chromium and improve the working environment in this sector. PFOS containing performance chemicals are also possibly used in copper plating, nickel plating, tin plating, plating plastic, and plating with precious metals.

PFOS use in metal plating in closed loop systems is listed as an acceptable purpose, and use in hard metal plating and decorative metal plating as a specific exemption. Therefore, countries can register for this use and several countries have already registered.

The main stakeholders to monitor the import and presence of PFOS in PFOS containing performance chemicals are customs and in particular the competent authority, which controls the plating industries. The association of metal/plastic plating industry and individual metal and plastic plating industries would be informed and encouraged to participate in a survey of the presence of PFOS and related chemicals in mist suppressant. Samples can be taken at the respective industries.

Other relevant industrial uses of PFOS having exemptions

PFOS and related chemicals used in photo imaging, photo resist and anti-reflective coatings for semi-conductors, and as etching agent for compound semi-conductors and ceramic filters have already been asked for as exemptions by several countries.

The main stakeholders to monitor the import and presence of PFOS in PFOS containing performance chemicals for these uses are customs and in particular the competent authority controlling these industries. From the industrial side, the relevant association and individual facilities would be informed and asked for information. Samples might be provided directly by the industrial associations or individual companies.

Other industrial uses with specific exemptions, but considered less relevant

Other industrial uses considered less relevant today are: treatment of paper, carpets, textiles, and leather; and PFOS derivatives that may be used as surfactants in the oil and gas industries to enhance oil or gas recovery in wells, as evaporation inhibitors for gasoline, as jet fuel, and hydrocarbon solvents. These uses are listed as specific exemptions and countries can register. However, for these uses, alternatives are available and already used. Since alternatives are often persistent chemicals they also could be assessed.

The related industries include the oil and gas industries, carpet industries, paper industry, textile industry, and leather industry. The main stakeholders to monitor the import and presence of PFOS and related substances in these industries are the industry (compliance) and customs (enforcement), and in particular the competent authorities responsible for supervision of these industries. Additionally, the industrial stakeholders would be included in the monitoring. Samples might be received from the mentioned stakeholders.

Aviation hydraulic fluids

Hydraulic oils containing PFOS have been used as an anti-erosion additive in civil and military airplanes since the 1970s to prevent evaporation, fires, and corrosion. This use of PFOS is listed as an acceptable purpose. Therefore, countries can register for this use.

The main stakeholders to monitor the import and presence of PFOS in aviation hydraulic fluids are customs, and in particular the competent authorities responsible for repair shops at airports and military air bases. Industrial stakeholders are airlines and workshops at airports using hydraulic oils for airplanes. Other stakeholders may include the military air force of the country and possibly other air forces stationed in the country. Samples might be received from the mentioned stakeholders.

Insect baits and insecticides

A PFOS related substance (sulfluramid⁶⁵) is used as insecticide against ants, cockroaches, termites, etc. The use for control of leaf-cutting ants is listed as an acceptable purpose and the use to control red fire ants and termites is listed as a specific exemption.

The main stakeholders to monitor the import and presence of PFOS related chemicals in insecticides are customs and the Ministry of Agriculture. Competent authorities could check for the presence of sulfluramid containing insecticides at pesticide producers, formulators, and in stores selling pesticides. Samples might be received from these stakeholders or purchased on the market.

Articles treated with PFOS and related chemicals

A part of PFOS, PFOS related chemicals and other PFCs might enter a country by impregnated products (see *PFOS Inventory Guidance*², Sections 2.4 and 5). This includes articles currently produced and articles in use (see section below).

Currently these articles are not labelled to indicate that they contain PFOS or other PFCs (for details on labelling approach see “POP labelling Guidance” (Stockholm Convention 2012⁶⁶)). Therefore, it is currently not possible to discover such articles by labels.

While the impregnated articles listed above are currently not labelled to contain PFOS or other PFCs, an indication for furniture, carpets, textile, leather, stone or other fabrics that possibly contain PFOS or other PFCs is a “stain resistant” label or advertisement for this property. For paper and paperboards, an indication for possible use of PFOS and other PFCs containing coatings are properties of water, oil, and grease resistance.

The main stakeholders to monitor the import and presence of articles impregnated with PFOS and related chemicals are customs and market surveillance authorities. The industrial stakeholders are companies producing, importing/exporting, or marketing these articles and products. Samples might be received from these stakeholders or purchased on the market.

These articles might include:

Synthetic carpets

A large share of synthetic carpets has been treated with PFOS related substances and other PFCs for stain resistance. For details see Section 2.1.3 of “Guidelines on BAT and BEP for the production and use of PFOS and related chemicals”

Textiles

PFOS and other fluorinated surfactants and polymers have been used to treat textiles and leather to provide oil and water repellency and soil and stain release properties. For details see Section 2.1.2 of “Guidelines on BAT and BEP for the production and use of PFOS and related chemicals”

Furniture

In particular couches, chairs and other furniture with potentially stain resistant surfaces.

See Chapter 2 PFOS BAT/BEP Guidelines⁵

⁶⁵ CAS: 4151-50-2; N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonamide

⁶⁶ Guidance on labelling of products or articles that contain new POPs or use new POPs during manufacture – initial considerations.

Paper

PFOS and other PFCs containing chemicals were/are used in food contact paper to provide oil, grease and water repellence (see Box A-2, below). PFOS derivatives, such as N-Me-FOSE and N-Et-FOSE was previously marketed under the tradename Scotchban (by 3M) and used to impregnate paper for e.g. margarine. While these applications seems to have been phased out in European countries, these and other PFOS based chemicals (e.g. SN-diPAPs also called SamPAPs, Trier 2011a and Benskin 2012)⁶⁷ were until recently sold in China, as industrial blends for paper coating purposes (Trier 2011). The industrial blends contained considerable amounts of PFOS impurities.

Box A-2: Some categories of food contact paper/packaging possibly using PFOS or other PFCs for oil, grease, or water repellency

- Wrapping paper used for fast food
- Burger boxes, pizza boxes
- Popcorn bags
- Muffin paper cups
- Baking paper, microwave paper
- Paper coffee cups
- Disposable crockery
- Cake and biscuit boxes (long-time storage of fatty foods)
- Sandwich wrapping paper (to wrap lunch boxes)
- Chewing gum cardboard boxes
- Other food packaging

Leather

See Section 2.1.2 of Guidelines on BAT and BEP for the production and use of PFOS and related chemicals

Further uses of PFOS in products and articles considered less relevant

Some other former PFOS uses that are not considered to be of priority today include:

- Industrial and household surfactants
- Paint and varnishes
- Toner and printing ink
- Sealants and adhesive products

The use of PFOS and related chemicals in these applications is not exempted and is therefore prohibited by the Convention. However, a country might decide to also assess the current status of the presence of PFOS in these applications and to ensure that PFOS is not used and additionally to evaluate what alternative chemicals are currently used including their environmental/health performance. For a more detailed description of these (former) PFOS applications, see “PFOS inventory guidance”². Samples might be received from stakeholders or purchased on the market.

⁶⁷ Trier X, Granby K, Christensen JH (2011a) Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging, Environ. Sci. Pollut. Res. 18, 1108-1120.

Monitoring of PFOS in articles in use (stocks)

The historic production of PFOSF from 1970 to 2002⁶⁸ is estimated to be approximately 96,000 tonnes and 26,500 tonnes of related production wastes⁶⁹. A large share of the produced PFOS and related chemicals was applied for surface treatment of carpets, textiles, paper, leather, and furniture. Therefore, the stock of PFOS and related chemicals in use and in particular deposited in landfills might have major relevance (in particular when considering the minor use volume today). Therefore, monitoring efforts need also to consider the stocks of articles currently in use. The same articles mentioned in above section “PFOS and related chemicals in production and as products” might be considered for the assessment of stocks. An overview on sectors might have been gained in the development of the PFOS inventory.

Samples might be taken from private households and businesses (e.g. carpets from hotels). Also samples might be purchased on the second-hand market.

Monitoring of PFOS in reuse and recycling

The “PFOS Inventory Guidance” considers carpet recycling as one inventory activity. Other articles potentially in recycling or reuse (possibly) treated with PFOS and related substances are textiles, paper, leather, and (textiles/leather on) furniture. Of these former relevant PFOS uses, the recycling of furniture and leather seems to be of minor relevance. Paper is recycled to a high degree in some countries, but due to the rather short use phase the paper formerly impregnated largely before 2002 (when 3M stopped such PFOS use) has entered the recycling chain some years ago.

The main stakeholders to monitor the recycling of PFOS containing carpets (and possibly other materials) are the competent authorities in the waste management sectors and factory inspection. Industrial stakeholders are the carpet (recycling) industry. Stakeholders for the monitoring of reuse of furniture impregnated with PFOS and related chemicals are market surveillance authorities in cooperation with second-hand furniture retailers. Samples might be taken from recycling facilities (e.g. for carpets or paper) and might be purchased on the second-hand market.

PFOS in biosolids and sludges

Sewage sludge and related biosolids are a final sink for a range of old POPs (e.g. PCB, PCDD/PCDF, and HCB) where, for some countries, regulation limits exist. Also, newly listed POPs – in particular PFOS and POP-PBDEs – are detected in sewage sludge/biosolids and in sediments (Benskin et al. 2012). The application of PFOS contaminated biosolids (originating from wastewater treatment plants related to PFOS/PFC productions⁷⁰ and industrial use) on agricultural areas have resulted in large scale contaminated sites, e.g. in Germany and the USA (Decatur Alabama)⁷¹ including groundwater and drinking water contamination. In the German case, PFOS/PFOA containing sludge has been imported into the country (Germany) and by further application as biosolid has resulted in large contaminated sites and the contamination of drinking water for approximately 5 million

⁶⁸ In 2002, 3M ended PFOS production.

⁶⁹ Paul AG, Jones KC, Sweetman AJ (2009) A First Global Production, Emission, And Environmental Inventory for Perfluorooctane Sulfonate. *Environ Sci Technol.* 43, 386-392.

⁷⁰ Oliaei F, Kriens D, Weber R, Watson A (2012) Assessment of PFOS and PFC pollution from a PFC production plant in Minnesota (USA). *Environ Sci Pollut Res Int.* DOI 10.1007/s11356-012-1275-4.

Oliaei F, Kriens D, Weber R. (2010) Discovery and investigation of PFOS/PFCs contamination from a PFC manufacturing facility in Minnesota – environmental releases and exposure risks. *Organohalogen Compounds* 72, 1338-1341. <http://www.dioxin20xx.org/pdfs/2010/10-1507.pdf>

Oliaei F, Kriens D, Weber R, Watson A (2012) Assessment of PFOS and PFC pollution from a PFC production plant in Minnesota (USA). *Environ Sci Pollut Res Int.* DOI 10.1007/s11356-012-1275-4.

⁷¹ USEPA <http://www.epa.gov/region4/water/PFCindex.html>

inhabitants.⁷²

Therefore, the use and import of biosolids might be a relevant source of PFOS/PFCs. Limit values of 100 µg PFOS+PFOA/kg (0.1 ppm) have been set e.g. in Germany by the [fertilizer ordinance](#)⁷³.

The customs would monitor the import of biosolids/organic fertilizers in cooperation with the agricultural ministry, which controls and monitors the overall use of sewage sludge and other biosolids in the country. Companies exporting or importing biosolids/organic fertilizer need to guarantee certain pollutant levels including (new) POPs and heavy metals. Samples might be received from mentioned stakeholders and might be sampled directly from sewage treatment plants. PFOS/PFC levels in sewage sludge can reveal and direct to point sources.

PFOS in feed, food and drinking water

The monitoring of feed, food and drinking water goes above the scope of this guidance and matrices are not covered by described methodologies. Due to the relevance for human exposure these articles are shortly mentioned here.

Food, feed and drinking water can in particular be contaminated with PFOS and related substances in connection with contaminated sites of former PFOS production, use and disposal. This includes e.g. lakes and rivers with elevated PFOS levels, fruits and vegetables from areas with soil and ground water is contaminated. Also drinking water can be contaminated with PFOS in areas with polluted ground water or surface water. If a country decides to include feed, food or drinking water into the monitoring of PFOS containing articles and products then the development of the monitoring concept should be linked with the development of the inventory of PFOS contaminated sites (developed during the NIP update). A first priority selection of samples can be done based on the findings of the PFOS contaminated site inventory. Samples might be received from stakeholders, purchased on the market or taken from households.

⁷² Kröfges P, Skutlarek D, Färber H, Baitinger C, Gödeke I, Weber R (2007) PFOS/PFOA Contaminated Megasites in Germany Polluting the Drinking water Supply of Millions of People. [Organohalogen Compounds 69, 877-880](#).

⁷³ Düngemittelverordnung 16. December 2008 (BGBl. I S. 2524), last modified 23. April 2012 (BGBl. I S. 611).

Annex 1–B: POP–PBDEs in articles and products⁷⁴

Since production of c-PentaBDE and c-OctaBDE is considered to have stopped in 2004, the monitoring can largely concentrate on articles and products in use, recycling, and end-of-life.

For c-OctaBDE, the material flow with the largest amount of c-OctaBDE content are certain polymers used in Electrical and Electronic Equipment (EEE) and related Wastes (WEEE).⁷⁵ Large amounts of EEE and WEEE were and are exported from industrial countries with former major use of c-OctaBDE (e.g. USA and Europe) to developing countries. Furthermore, polymers from recycling of WEEE are partly sent for recycling to developing/transition countries (e.g. China or India). Recent studies have shown that recycled polymers containing PBDE have been used to produce articles for which no flame retardancy is required including, for example, children's toys, household goods, and video tapes.⁷⁶ This shows that the flows of polymers containing PBDEs for recycling are not well controlled and need to be monitored and better managed.

For c-PentaBDE, the main use was PUR foam in transport (cars, buses, trains, etc.) and furniture and for some regions possibly insulation in construction.

Therefore, the reuse and recycling of these two major material flows need to be monitored.

Details on the POP-PBDE material flows are given in the "POP-PBDE inventory Guidance"³ and "POP-PBDE BAT/BEP Guidelines"⁴.

Considering these major uses of c-PentaBDE and c-OctaBDE, the following reuse of articles and goods and recycling flows would be assessed (in the country and in imports):

POP-PBDEs as and in chemical products

Although production has officially stopped, some companies still offer c-PentaBDE (CAS 32534-81-9)⁷⁷ and c-OctaBDE (32536-52-0) for sale in the public domain although production and marketing is banned under the Convention. Therefore, illegal trade of these chemicals might still take place. Companies offering POPs are listed in Annex of „POPs Customs Control Guidance“⁷⁸.

C-DecaBDE is still produced as flame retardant. The production of c-DecaBDE by bromination of diphenylether has POP-PBDEs as intermediates. Therefore c-DecaBDE could contain POP-PBDE as contaminant and could be monitored. C-DecaBDE debrominates under various conditions (UNEP 2010c). Therefore articles containing c-DecaBDE and articles recycled from c-DecaBDE containing materials would be monitored for POP-PBDE.

Second hand EEE in import and on the local market

Polymers of used EEE (produced before 2005) can contain POP-PBDE⁷⁹. The most relevant WEEE fractions are Cathode Ray Tube (CRT) housing from TVs and computers. Imported used EEE is, in

⁷⁴ Production of HBB stopped in 1976 and it is therefore not considered for the regular monitoring of articles.

⁷⁵ See Section 4 of Guidance for the inventory of PBDEs listed under the Stockholm Convention (Draft).

⁷⁶ UNEP (2010) Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. ([UNEP/POPS/POPRC.6/2](#))

⁷⁷ Examples include: Shi Jiazhuang Luchi Chemical Co., Ltd.; Yick-Vic Chemicals & Pharmaceuticals (HK) Ltd; Weifang Sinobrom Imp & Exp Corp.,Ltd.; Tianjin Chengyi International Trading Co., Ltd.; Dalian Jinbosheng Chemical Co., Ltd; Jia Xiang Industry Co.,Ltd; XiaoShuLin, HeBei District, TianJin; Shenyang Jiutongyuan Chemicals Co., Ltd; Shijiazhuang Hengsikai Chemical Imp&Exp Co.,Ltd; and Shijiazhuang Kunli Chemical Co. Ltd; Zenith Chemicals Ltd. (HK).

⁷⁸ Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft)

⁷⁹ Plastic in electronics produced from 2005 on can contain trace amount of c-OctaBDE from recycling of c-OctaBDE containing polymers.

many countries, subjected to assessment of their functionality to avoid illegal import of WEEE⁸⁰. Therefore, customs are already monitoring used electronics. Within this monitoring, screening of bromine for indication of POP-PBDE might be performed. However, since other brominated flame retardants are mainly present in today's used electronics, confirmation analysis would need to be considered. Samples might be received from stakeholders, purchased on the market, from households or end-of-life treatment facilities.

Import of Waste Electrical and Electronic Equipment (WEEE)

The largest amount of POP-PBDEs of c-OctaBDE is present in WEEE, in particular Cathode Ray Tube (CRT) housing from TVs and computer monitors and office equipment. WEEE might be imported into a country, for example, as a good for recovery of metals. Considering the legislation of a country and the Basel Convention rules, such imports might be legal.

Depending on further treatment of this WEEE and in particular the treatment of the polymer fraction, this POP-PBDE-containing material can cause environmental pollution (e.g. from the practice of open burning) or hazards if recycled into sensitive products (table A-1). Therefore, competent authorities and industries treating the WEEE need to assure the appropriate management and treatment of the associated polymer material of such WEEE imports (see Chapter 4 of the *"PBDE BAT/BEP Guidelines"*⁴). If the polymer is subjected to further recycling, the competent authority would monitor or ask the companies for monitoring data and assure pollutants like POP-PBDEs are separated according to the recommendations of the Conference of Parties if no exemption for recycling is granted. If the country has asked for exemption of recycling PBDE containing materials, it should take care that, in particular, such polymers are not recycled into sensitive uses (see table also Chapter 4 of *POP-PBDE BAT/BEP Guidelines*⁴).

WEEE plastic for recycling

The polymer fractions from recycling of WEEE are the most relevant recycling material flow possibly containing POP-PBDEs. Mainly ABS plastic but also mixed WEEE plastic fractions might be impacted. Such polymer fractions are partly exported – often from industrial countries to developing countries for material recycling purposes to produce new plastic products. Such polymers might be plastic flakes from WEEE shredders or pelletised plastic. The monitoring for the recycling of this polymer might also include, in addition to POP-PBDEs, other RoHS Directive⁸¹ relevant substances.

**Table A-1: Examples of sensitive use areas*
where POP-PBDE-containing recycled polymers must not be used****

Some sensitive uses of plastic

- Toys
- Food packaging; food containers
- Kitchen equipment
- Refrigerator interior***; freezer interior***
- Water tanks (in particular tanks used for drinking water)
- Water pipes (in particular drinking water pipes)
- Silos, storage, and piping for food and animal feed

⁸⁰ Basel Convention (2011) Technical guidelines on transboundary movements of e-waste, in particular regarding the distinction between waste and non-waste. 15. July 2011, UNEP/CHW.10/INF/5.

⁸¹ Directive on the restriction of the use of certain hazardous substances in EEE 2002/95/EC.

- Polymer parts with direct contact
- Furniture, handles of tools, doors, etc.

* In such applications generally recycled polymer fractions containing heavy metals, or critical softeners, brominated flame retardant, phosphor organic flame retardant or other critical chemical should not be used.

** The list provides key examples of sensitive uses and is not considered comprehensive.

*** The recycling of polymers from WEEE plastics containing no critical chemicals is encouraged following the cradle to cradle principle, e.g. polymers from refrigerators/fridges to refrigerators/fridges.

Used cars, buses, and other vehicles (produced before 2005)

C-PentaBDE has been applied in cars, buses, and trucks for treating polyurethane foam in e.g. the upholstery of seats, headrests, or armrests until 2004 in some regions. C-OctaBDE has been used to a minor extent in dashboards and other plastic parts until 2004 in some regions.

Depending on the phase-out of POP-PBDEs in different regions, vehicles produced within a region can be regarded as not or low⁸² impacted:

- In Europe: POP-PBDEs have been used until late 1990s
- In the US: POP-PBDE have been produced until 2004
- In Japan: POP-PBDE have been used until late 1990s
- In China: POP-PBDE production and use from c-PentaBDE is unclear

Vehicles produced until these dates in these countries/regions can contain POP-PBDEs.⁸³ Therefore, POPs-BDEs are imported to developing countries with second-hand vehicles containing such treated polymers.

Currently there are no data on which producers have used POP-PBDEs in which series. Therefore, currently only screening of the vehicles by non-destructive XRF in current used vehicles (or screening of end-of-life vehicles) could clarify the presence/absence of POP-PBDEs/BFRs in the respective vehicles. A positive detection of bromine in PUR foam (seat, headrest, etc.) in vehicles produced before 2005 is a strong indication of the presence of c-PentaBDE. A confirmation analysis by GC/ECD or GC/MS can then be performed.

Furniture and mattresses containing PUR-foam (produced before 2005)

The use of c-PentaBDE (and other flame retardants) in furniture depends on the flammability standard of a country (Shaw et al. 2010)⁸⁴. Due to flammability standards for furniture in the US and UK in particular furniture in North America and UK are often flame retarded. Therefore older furniture in these region/countries may contain c-PentaBDE (or other flame retardants).

The extent of furniture exported from North America or UK for re-use to other regions has not been assessed and need to be considered as a possible source for c-PentaBDE input for other countries.

⁸² Plastic parts from vehicles are partly recycled and could have been used in new vehicles.

⁸³ Please note that Japanese and European car manufacturers have also produced within the US and therefore these cars produced in the US might contain POP-PBDEs until 2005.

⁸⁴ Shaw SD, Blum A, Weber R, Kannan K, Rich D, Lucas D, Koshland CP, Dobraca D, Hanson S, Birnbaum LS. (2010) Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? [Reviews on Environmental Health 25\(4\) 261-305](#).

Mattresses have to a minor extent been flame retarded with c-PentaBDE (in particular from institutions like prisons, military, hospitals or hotels) (see POP-PBDE BAT/BEP Guidelines). Samples can be taken from mattresses which in field screenings were bromine positive.

These applications can be sampled easily in end-of-life phase.

PUR foam in other applications

Also other PUR-foam applications have partly been treated with c-PentaBDE such as various baby products ([Stapleton et al. 2011](#)) pillows or for packaging. PentaBDE was also used in rigid PUR foam in construction. Therefore (formerly used) foams in construction might contain POP-PBDE.

These applications can be sampled in the end-of-life phase.

Textiles and rubber

PentaBDE have been used⁸⁵ in limited quantities for the treatment of textiles for uses including back-coating, for curtains and for functional textiles (UNEP 2009). Functional textiles might be screened for their bromine content.

PentaBDE has also been used in rubber for e.g. conveyor belts and other minor uses. If a country has larger use of rubber conveyor belts also these could be monitored.

Articles produced from recycled plastic

Currently no regulation exists on the labelling of articles produced from recycled polymers. Therefore these materials can currently only be monitored by analytical screenings. The main stakeholders to monitor the import and presence of PBDE containing articles made from recycled polymers are customs and authorities for market surveillance. Industries using recycled polymers from WEEE or transport would monitor for POP-PBDE and report to the environmental ministry or NIP coordinator on levels of POP-PBDEs.

The articles can be assessed in a similar way as the polymers described above. A similar screening approach as for other materials (XRF screening combined with confirmation analysis) might be applied. Sliding spark spectroscopy is not sensitive enough (1000 ppm bromine) for such a screening. Possible articles for a screening are, for example, those listed in the negative list (see Box 3, above).

PUR foam for recycling

PUR foam from end-of-life products (ELV vehicles, furniture, mattresses) might be gathered for recycling purposes. Such PUR foam for recycling might be used in the country, exported or imported from other countries.

Articles produced from recycled PUR foam

PUR foams for recycling might be used in different new articles and products.

Carpet re-bond: Large scale recycling of PUR foam into carpet padding/re-bond is currently practised in the US and Canada (Luedeka 2011, see PBDE BAT/BEP Guidance Chapter 6). The extent of this recycling activity for other regions is unknown but appears to be limited (DiGangi et al. 2011). If carpet rebond is imported from this region, it might contain POP-PBDEs. Relevant exposure of workers in PUR recycling and carpet installers has been demonstrated in a first study from the US (Stapleton et al. 2008) and there are obvious risks of further exposure of consumers.

Other uses: While the majority of polyurethane foam scrap is processed into carpet rebond (in the U.S. market), scrap can also be shredded and used as packaging and stuffing for pillows, pet bedding,

⁸⁵ C-DecaBDE and HBCDD are still used in the impregnation of textiles.

insulation and stuffed animals for kids. Foam scrap might also be used for some furniture cushioning, sound insulation or gymnastic mats or (school) bus seats (UNEP 2010b, USEPA 1996, Zia et al. 2007).

Regrinding: PUR foam is partly grinded to ultrafine powder and added to the virgin material in the manufacture of new foams. If POP-PBDE-containing PUR foam is used then also new PUR foam can become polluted.

PBDE in biosolids, sewage sludge and industrial sludges

Sewage sludge and related biosolids are final sinks for a range of old POPs (e.g. PCB, PCDD/PCDF, HCB) where, for some countries, regulation limits exist. Also, newly listed POPs – in particular PFOS and POP-PBDEs – are detected in sewage sludge/biosolids. PBDE contaminated biosolids and sewage sludge might originate from wastewater treatment plants related to (former) PBDE production and industrial use). Companies exporting or importing biosolids/organic fertilizer need to assure the origin of the biosolids and guarantee certain pollutant levels including (new) POPs and heavy metals.

PBDEs in feed and food

The monitoring of feed and food goes above the scope of this guidance and matrices are not covered by described methodologies here. Due to the relevance for human exposure these articles are shortly mentioned here.

Food and feed can in particular be contaminated with POP-PBDE in connection with contaminated sites of former POP-PBDE production, use and disposal. This includes e.g. fish from lakes and rivers with former PBDE intake, eggs and milk from areas where formerly PBDE contaminated sludges or bio-solids have been applied or landfill where POP-PBDE containing materials has been disposed. If a country decides to include feed and food into the monitoring of PBDE containing articles and products then the development of the monitoring concept would best be linked to the development of the inventory of POP-PBDE contaminated sites. A first priority selection of samples can be done based on the findings of the POP-PBDE contaminated site inventory then.

Annex 1–C: PeCBz and other unintentional POPs (HCB, PCDD, PCDF and PCB) as unintentional trace contaminants in chemicals, chemical in mixtures, and articles

Pentachlorobenzene (PeCBz) is the only newly listed unintentionally produced POP in SC Annex C. Similar to HCB, it is also listed as an intentionally produced POP in SC Annex A. Today, the relevance of PeCBz and HCB are rather as trace contaminants in products than from intentional production. However, production of PeCBz and HCB also still might take place (see below).

Since the different unintentionally formed POPs are normally formed in most processes at the same time, it is reasonable not to solely address PeCBz in suspected chemicals and articles, but to also address and monitor all listed unintentionally produced POPs in screenings of unintentional produced POPs in products and articles. The necessity to screen PCDD/PCDF in products was recently been highlighted by discovery of extreme high levels of PCDD/PCDF (522 µg TEQ/kg) in Chinese chloranil with PCDD/PCDF levels 35 times above the low POPs threshold of the Basel Convention for wastes (Liu et al. 2011).⁸⁶ The estimated total PCDD/PCDF content of this currently marketed chemical from China alone was estimated to 1044 g TEQ which is about 10% of China's total PCDD/PCDF inventory, but present directly in treated consumer products. PeCBz, HCB, and PCB were also detected in these chemicals in relevant concentration (Liu et al. 2011).

Unintentionally produced POPs present as unintentional trace contaminants in chemicals, mixtures, and articles can be addressed by lists of chemicals, mixtures, and articles which, from past analysis, have been found to contain these chemicals or are suspected to contain unintentionally produced POPs.

PeCBz and HCB as product

Some companies still offer HCB and PeCBz although production and marketing is banned under the Convention. Therefore, trade of these chemicals might still take place. Companies offering HCB and PeCBz are listed in the Annexes of the POPs Customs Control Guidance⁸⁷.

PeCBz, HCB, and PCDD/PCDF in pesticides and related organochlorine chemicals

Some pesticides are known to contain or form relevant levels of HCB during production and therefore can be suspected also to contain PeCBz. These include, for example, PCNB (CAS No 82-68-8), PCP (CAS No 87-86-5), dimethyltetrachloro terephthalate dacthal (CAS No 1861-32-1), chlorothalonil (CAS No 1897-45-6), and dicloram (CAS No 1918-02-1) (Tobin, 1986).⁸⁸

While releases from production in industrial countries have been reduced, production capacity has shifted to developing/transition countries like China, India, and others. Recent screening of contemporary used pesticides in Australia (Holt et al. 2010) and Chloranil in China (Liu et al. 2011) revealed that PCDD/PCDF were present in all tested products and that some products contained high levels of PCDD/PCDF.

In the updated UNEP standardized toolkit for Dioxin and Furan releases (Stockholm Convention 2012), a range of chemicals are listed which are known or suspected to contain PCDD/PCDF. Since unintentionally produced POPs are normally formed in parallel, these chemicals can be suspected to also contain PeCBz, HCB, and PCB. This list might therefore be used for monitoring of PeCBz and other unintentionally produced POPs in products and articles.

⁸⁶ Liu W, Tao F, Zhang W, Li S, Zheng M (2011) Contamination and emission factors of PCDD/Fs, unintentional PCBs, HxCBz, PeCBz and polychlorophenols in chloranil in China. *Chemosphere* 86, 248-251.

⁸⁷ Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft).

⁸⁸ Tobin P (1986) Known and potential sources of hexachlorobenzene. In: Morris, C.R.; Cabral, J.R.P. Hexachlorobenzene: Proceedings of an International Symposium. Lyon, IARC Sci. Publ. 77, 1-12.

Samples might be gathered from stakeholders or purchased from the market.

PeCBz, HCB in pigments and tetrachlorophthalic anhydride

Some pigments based on tetrachlorophthalic anhydride contain relatively high levels of HCB. They can also be suspected to contain PeCBz and possibly other unintentionally formed POPs. Japan has informed the Conference of Parties (COP4) of the Stockholm Convention of the high HCB content and suggested BAT levels for HCB in these pigments and in tetrachlorophthalic anhydride ([Government of Japan 2006](#)⁸⁹ and [2007](#)⁹⁰). Pigments reported to contain HCB could be monitored for PeCBz and other unintentionally produced POPs (Table A1-2).

Table A1-2: Pigments known to contain HCB, and possibly PeCBz or other unintentionally produced POPs

<i>Pigment/chemical</i>	<i>CAS Registry Number</i>
Pigment Yellow 110	5590-18-1
Pigment Yellow 138	30125-47-4
Pigment Green 7 ⁹¹	1328-45-6 and 1328-53-6
Pigment Green 36	14302-13-7
Solvent Red 135	20749-68-2 and 71902-17-5
Tetrachlorophthalic anhydride	117-08-8

Unintentionally produced POPs in articles

Articles where chemicals and mixtures have been added or included known or suspected to contain unintentionally POPs could then also contain unintentionally produced POPs, for example, the above mentioned pigments are used in a wide range of products such as plastic, bank notes, and paints. Potentially unintentionally POPs containing biocides are used for treatment of wood or leather (e.g. PCP) or in soap and toothpaste (e.g. triclosan).

PeCBz and HCB in chlorinated solvent

During production of certain chlorinated solvents, high amounts of unintentional HCB and PeCBz can be formed (UNEP, 2010).⁹² These include tetrachloroethene (CAS: 127-18-4), trichloroethene (CAS: 79-01-6), and tetrachloromethane (CAS: 56-23-5). The largest part of the

⁸⁹ Government of Japan (2006) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product November 2006. Submission to COP3.

⁹⁰ Government of Japan (2007) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product. April 2007. Submission to COP3.

⁹¹ Due to its stability, Pigment Green 7 is used in inks, coatings, and many plastics. In application, it is transparent. The pigment is insoluble and has no tendency to migrate in the material. It is a standard pigment used in printing ink and packaging industry. It is also allowed in cosmetics except those used around the eyes, and is used in some tattoos.

⁹² UNEP (2010) Additional consideration of new persistent organic pollutants: pentachlorobenzene. Stockholm Convention document for 6th POP Reviewing Committee meeting ([UNEP/POPS/POPRC.6/INF/21](#)) Geneva 11-15. October 2010.

unintentionally produced POPs is normally separated in the production by a distillation step from the marketed solvent and remain as heavy distillates (Jacob et al. 1986). It has been reported that these deposits also contain PeCBz (UNEP et al. 2010⁹³; Weber et al. 2011⁹⁴). There is a scarcity of data on the content of HCB and PeCBz in chlorinated solvents (UNEP 2010⁹⁵). Therefore, screening of PeCBz, HCB, and possibly other unintentionally formed POPs in chlorinated solvents could be considered.

PCDD/PCDF and other unintentional POPs in biosolids/sewage sludge

Sewage sludge and related biosolids are sinks for unintentionally produced POPs (PCDD/PCDF, PCB, HCB, and PeCB) and newly listed POPs (PFOS, POP-PBDE). In some countries, regulation limits exist for POPs in respect to the application on agricultural areas and pasture areas to prevent the contamination of food. Biosolids and organic fertilizers are also traded at the international level and control of POPs levels could be addressed with respect to imports, exports, and trade.

In a survey of German sewage sludges levels of PeCBz and HCB were relatively low (below 10 ng/g) and significantly lower compared to their brominated analogues hexabromobenzene and pentabromobenzene detected at an average concentration of 330 ng/g and 45 ng/g respectively (Kuch et al. 2005⁹⁶).

While formerly the broad use of PCP was the main contamination source of PCDD/PCDF in sewage sludge, today elevated levels of PCDD/PCDF in sewage sludges are mainly associated with industries such as the textile industry (Fuente et al. 2007⁹⁷)

Unintentionally produced POPs (PCDD/PCDF, PeCBz, HCB, PCB) in food and feed

Food and feed in particular can be contaminated with PCDD/PCDF and other unintentionally produced POPs in connection with historic releases of PCDD/PCDF, intentionally and unintentionally PCBs and other unintentionally produced POPs from industries, contaminated pesticides, or application of contaminated sludge.^{98,99} This includes, for example, fish from lakes and rivers or the sea with former PCDD/PCDF, PCB or other unintentionally produced POPs input.¹⁰⁰ Floodplains of such rivers can also be impacted by PCDD/PCDF and other unintentionally produced POPs with contamination of grazing cattle and related milk and meat.¹⁰¹ Furthermore, also relevant

⁹³ UNEP, OCHA, and EU Commission (2010) A Joint United Nations – European Commission Environmental Emergency Response Mission: Technical Scoping Mission Kalush Area, Ukraine March 2010.

⁹⁴ Weber R, Watson A, Malkov M, Costner P, Vijgen J (2011) Unintentionally produced hexachlorobenzene and pentachlorobenzene POPs waste from solvent production – the need to establish emission factors and inventories. *Organohalogen Compounds* 73, 2205-2208.

⁹⁵ UNEP (2010) Additional consideration of new persistent organic pollutants: pentachlorobenzene. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/21) Geneva 11-15. October 2010.

⁹⁶ Kuch B, Schneider C, Metzger JW, Weber R (2005) Hexabromobenzene and Pentabromophenol in German Sewage Sludge – Indication of Significant Commercial Use. *Organohalogen Compounds* 67, 434-437.

⁹⁷ Fuentes MJ, Font R, Gomez-Rico MF, Molto J (2007) Multivariate statistical analysis of PCDD/FS in sewage sludges from different areas of the Valencian Community (Spain). *Chemosphere* 67, 1423-1433.

⁹⁸ UNEP Stockholm Convention (2012) *ibidem*, Weber et al. (2008) Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. *Env Sci Pollut Res.* 15, 363-393.

⁹⁹ Birch GF, Harrington C, Symons RK, Hunt JW (2007) The source and distribution of PCDDs and PCDFs in sediments of Port Jackson, Australia. *Marine Pollution Bulletin* 54, 295-308.

¹⁰⁰ Assmuth T, Jalonon P (2005) Risks and management of dioxin-like compounds in Baltic Sea fish: An integrated assessment. *TemaNord* 2005:568

¹⁰¹ Schulz AJ, Wiesmueller T, et al. (2005) Dioxin concentration in cows' milk in dependence on feed and soil contamination. *Proc. Soc. Nutr. Physiol.*, 14, 52; Schulz AJ, Wiesmueller T, et al. (2005) Dioxin concentration

contamination are eggs and milk from areas where formerly PCDD/PCDF, PCB or other unintentionally produced POPs contamination has occurred.

If a Party decides to include food and feed into the monitoring of unintentionally produced POPs-containing articles and products, the development of the monitoring concept would be linked to the development of the inventory of PCDD/PCDF, PCB and other unintentional POPs contaminated sites. A first priority selection of samples can be made based on such an inventory. Monitoring could also include an assessment of the feed market.¹⁰² Furthermore, a monitoring concept could also address imported food and feed.¹⁰³

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in milk and tissues of cows and sheep related to feed and soil contamination. *J. Anim. Physiol. Anim. Nutr.* 89, 72-78; Kamphues et al. (2011) *Organohalogen Compd.* 73, 2040-2041.

¹⁰² Weber R, Watson A (2011) Assessment of the PCDD/PCDF Fingerprint of the Dioxin Food Scandal from Bio-Diesel in Germany and Possible PCDD/F Sources. [Organohalogen Compounds 73, 400-403](#).

¹⁰³ Hussain A, Dashti B, Gevaio B, Al-Wadi M, Brouwer A, Behnisch PA (2011) First Surveillance monitoring results of feed and food samples from markets in Kuwait from international origin for PCDD/PCDF/PCB-TEQ by DR CALUX. [Organohalogen Compounds 73, 2000-2003](#).

ANNEX 2 Instrumental analysis

The analytical conditions and chromatograms were provided from Prof. Dr. Dr. Takumi Takasuga (Shimadzu Techno Research, Kyoto, Japan)

Annex 2–A: GC/MS analysis of PBDE

PBDEs GC/MS conditions (example)

Table A2-1: GC/MS conditions for PBDE and HBB

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 (0 min) – 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	EI
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

PBDE masses and mass windows

Table A2-2: Masses of detected ions (m/z 's) for PBDE (HRMS masses; for LRMS reduced digits)

Compounds within GC time windows	Quantification	Confirmation
Tetrabromodiphenylether	485.7112	483.7132
Pentabromodiphenylether	563.6216	565.6197
Tetrabromo[¹³ 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 C ₁₂]diphenylether	577.6598	575.6618
Hexabromo[¹³ C ₁₂]diphenylether(M-2Br)	495.7357	493.7377
Heptabromo[¹³ 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 C ₁₂]diphenylether(M-2Br)	573.6462	575.6442
Perfluorokerosene	566.9665	
Octabromodiphenylether (M-2Br)	641.5145	639.5165
Octabromo[¹³ C ₁₂]diphenylether(M-2Br)	653.5546	651.5567
Perfluorokerosene	642.9601	
Nonabromodiphenylether (M-2Br)	719.4250	721.4230
Nonabromo[¹³ C ₁₂]diphenylether(M-2Br)	731.4651	733.4631
Perfluorokerosene	730.9537	
Decabromodiphenylether (M-2Br)	799.3335	797.3355
Decabromo[¹³ C ₁₂]diphenylether(M-2Br)	811.3737	809.3757
Perfluorokerosene	804.9505	

PBDE SIM Chromatogram

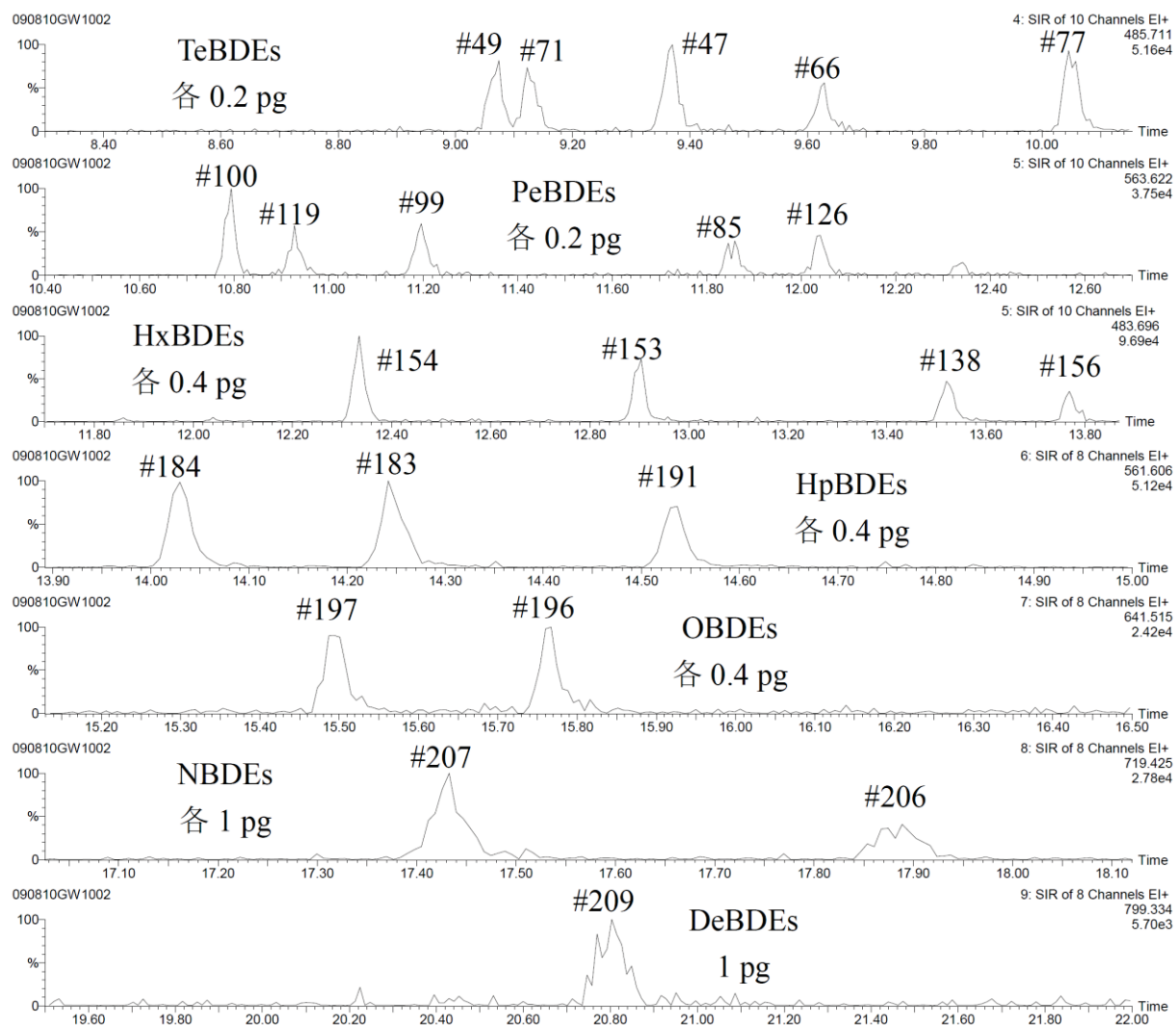


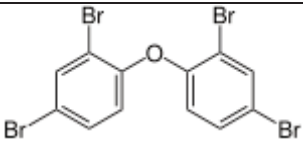
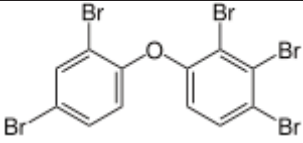
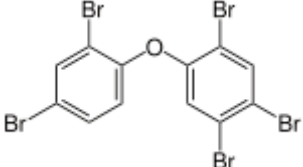
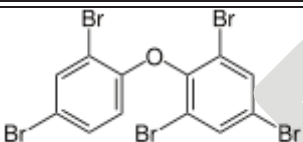
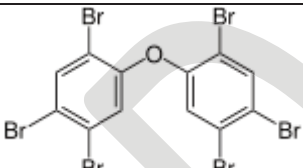
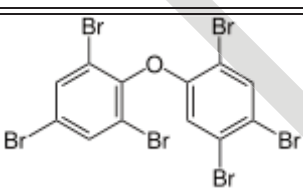
Figure A2-1: Chromatogram of tetraBDE to decaBDE

(Please note that only tetraBDE, pentaBDE, hexaBDE and heptaBDE are listed as POPs)

Major POP-BDE congeners in commercial mixtures

Table A3-1 and A3-2 list the major POP-PBDE in commercial PentaBDE and commercial OctaBDE present in articles where these mixtures have been applied (La Guardia et al. 2006)¹⁰⁴

Table A3-1: Major POP-PBDEs in commercial PentaBDE (La Guardia et al. 2006)

Composition of commercial PentaBDE			
Structure	Congener	Name	Fraction
	BDE-47	2,2',4,4'-tetra-bromodiphenyl ether	38–42 %
	BDE-85	2,2',3,4,4'-penta-bromodiphenyl ether	2.2–3.0 %
	BDE-99	2,2',4,4',5-penta-bromodiphenyl ether	45–49 %
	BDE-100	2,2',4,4',6-penta-bromodiphenyl ether	7.8–13 %
	BDE-153	2,2',4,4',5,5'-hexa-bromodiphenyl ether	5.3–5.4 %
	BDE-154	2,2',4,4',5,6'-hexa-bromodiphenyl ether	2.7–4.5 %

Note: Other congeners than mentioned above are only traces in concentration in commercial mixtures

¹⁰⁴La Guardia MJ, Hale RC, Harvey E (2006) Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures, Environ. Sci. Technol. 40, 6247–6254.

Table A3-2: Major POP-PBDEs and other PBDE congeners in commercial OctaBDE in treated articles (La Guardia et al. 2006)

Composition of commercial OctaBDE				
Structure	Congener	Name		Fraction
	BDE-153	2,2',4,4',5,5'-hexa-bromodiphenyl ether		0.15–8.7 %
	BDE-154	2,2',4,4',5,6'-hexa-bromodiphenyl ether		0.04–1.1 %
	BDE-171	2,2',3,3',4,4',6-hepta-bromodiphenyl ether		0.17–1.8 %
	BDE-180	2,2',3,4,4',5,5'-hepta-bromodiphenyl ether		n.d.–1.7 %
	BDE-183	2,2',3,4,4',5',6-hepta-bromodiphenyl ether		13–42 %
	BDE-196*	2,2',3,3',4,4',5,6'-octa-bromodiphenyl ether		3.1–10.5 %
	BDE-197*	2,2',3,3',4,4',6,6'-octa-bromodiphenyl ether		11–22 %
	BDE-203*	2,2',3,4,4',5,5',6-octa-bromodiphenyl ether		4.4–8.1 %

* Congeners not considered as POPs under the Stockholm Convention.

Note: Other congeners than mentioned above are only in trace concentrations

Annex 2–B: GC/MS analysis of HBB

GC/MS conditions HBB (example)

Instrument	Autospec Ultima (Waters/Micromass) GC:HP 6890 (Agilent)
Column	ENV-5MS 15 m × 0.25 mm I.D. (0.1 μm) (Kanto chemical) (5% Phenyl Polysilphenylene-siloxane)
GC prog.	120 °C (1 min) – 20 °C /min – 200 °C (0 min) – 10 °C /min – 300 °C (8 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	EI
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	M/ΔM > 10000 (10% Valley)

Table A2-4: Masses of detected ions (m/z 's) for HBB

	Quant.	Confirm.
Hexabromobiphenyl	627.5352	625.5372
Hexabromo[13C12]biphenyl	639.5754	637.5775
Hexabromo[13C12]diphenylether	655.5703	653.5723
Perfluorokerosene	642.9600	

HBB SIM Chromatogram

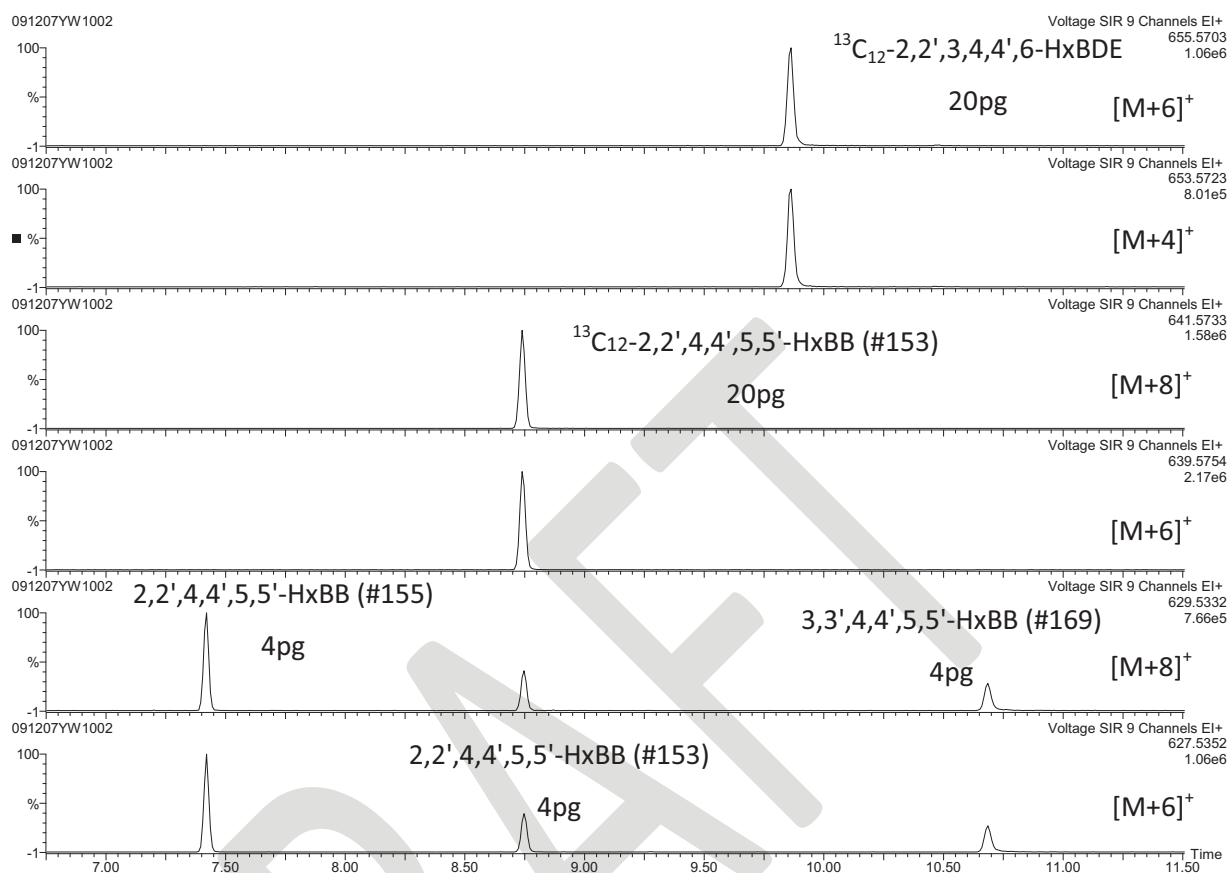


Figure A2-4: Chromatogram of native HBB congeners and $^{13}\text{C}_{12}$ -HBB

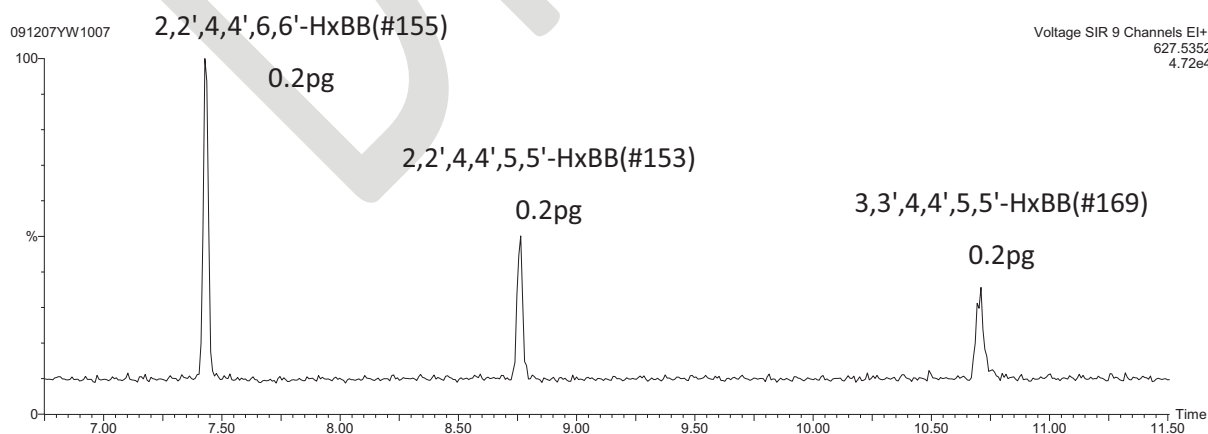


Figure A2-5: Chromatogram of native HBB congeners

Annex 2–C: GC/MS analysis of PeCBz, HCHs and basic pesticide POPs

GC/MS conditions PeCBz, HCHs and basic pesticide POPs (example)

MS Instrument	LRMS or HRMS
GC	HP 6890 (Agilent)
Column	DB-17HT 30 m x 0.32 mm I.D. (0.15 µm) (Agilent Technologies/J&W)
GC prog.	120°C (1 min)-20°C /min-160°C (0 min)-3°C /min- -220°C (0 min)-10°C/min-300°C (3 min)
Inj.	On Column
Guard col.	Deactivated capillary 0.5 m x 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	EI
Electron Voltage	30~40eV
Trap Current	500 µA
Accelerated Voltage	8 kV
Interface temp.	300°C
Ion source temp.	300°C
Detection	SRM (e.g. SIM)
Resolution	M/ΔM > 10,000 (10% Valley)

Table A2-4a?: Masses of detected ions (m/z 's) for PeCBz and $^{13}\text{C}_6$ -PeCBz

	Quant.	Confirm
Pentachlorobenzene	249.8492	251.8462
$^{13}\text{C}_6$ -Pentachlorobenzene	255.8693	257.8663
$^{13}\text{C}_{12}$ -4,4'-dichlorobiphenyl	234.0406	236.0376
Lock mass	254.9856	

Table A2-5: Ion masses for HCB and PeCBz determination

	Quantification	Confirmation
PeCB	249.8492	251.8462
$^{13}\text{C}_6$ -PeCB	255.8693	257.8663
HCB	283.8102	285.8072
$^{13}\text{C}_6$ -HCB	289.8303	291.8273

[M]⁺

Calibration curve

The concentration of PeCBz and HCB standard solutions prepared with nonane was ranged from 0.5 ng/mL to 1000 ng/mL gradually. The concentration of the internal substance in the standard solution for preparing the calibration curve was all set at 10 ng/mL for ¹³C₆-HCB and ¹³C₆-PeCBz and 25 ng/mL for ¹³C₁₂-PCB 70.

1 µL of sample solution is injected in the GC/MS operated in the SRM (SIM) mode. If the retention time of the HCB peak on the chromatogram was the same and the peak area ratio of the two monitor ions was equivalent to the area ratio of the isotope, it then was identified as HCB and its quantity was determined.

Chromatogram PeCBz (DB-17HT 30 m x 0.32 mm I.D. (0.15 µm))

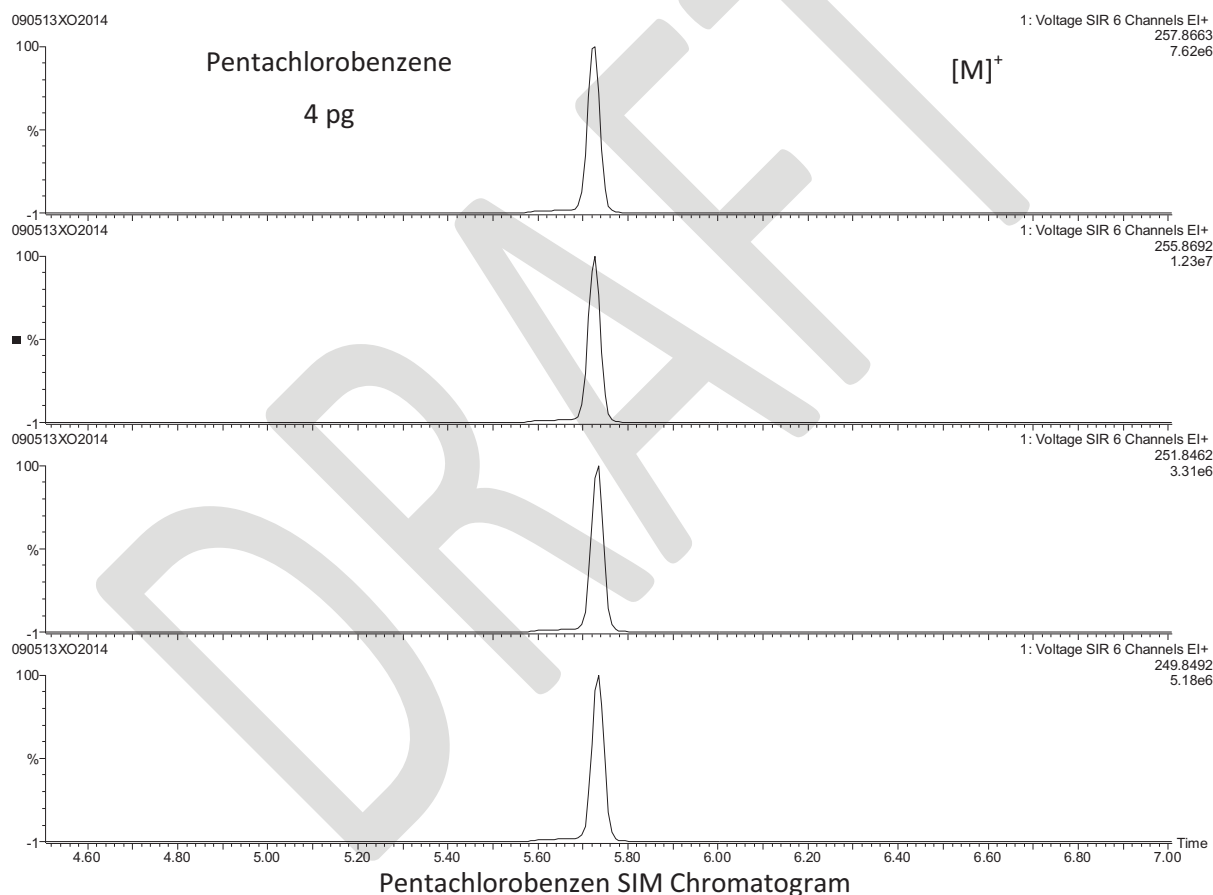
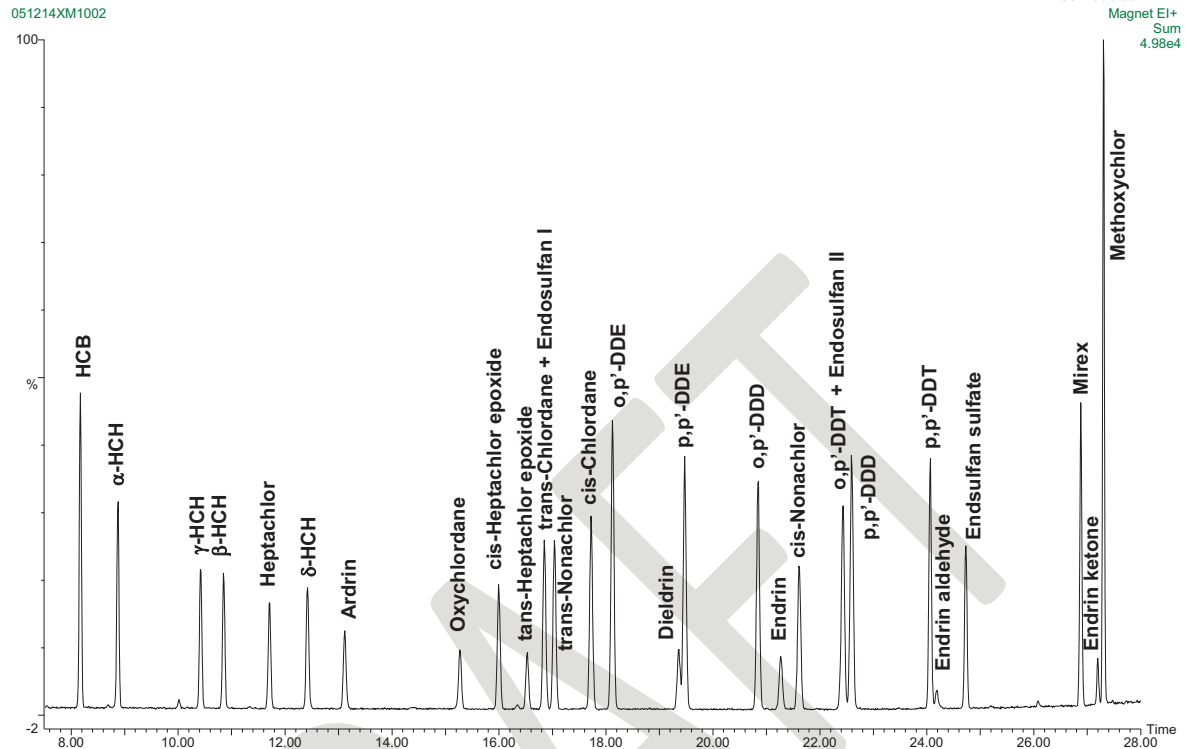


Figure A2-6: Chromatogram of PeCBz

Chromatograms HCHs, DDT (and degradation products) and other basic pesticide POPs

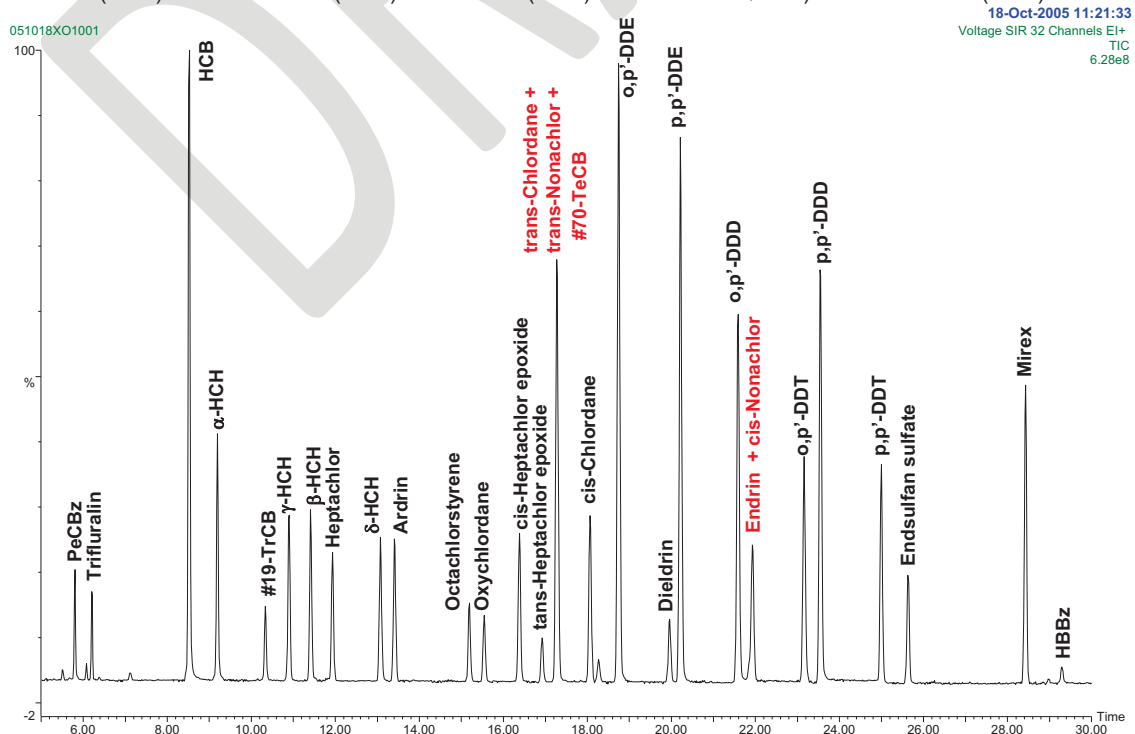
DB-17HT 30m, 0.32mm I.D., 0.15 μ m

120°C(1min)-20°C/min-160°C (0min)-3°C/min-220(0min)-10°C/min-300°C (3min)



BPX-50 30m, 0.32mm I.D., 0.15 μ m

120°C(1min)-20°C/min-160°C (0min)-3°C/min-220(0min)-5°C/min-260°C (0min)-10°C/min-300°C (3min)



Annex 2–D: LC/MS analysis of PFOS

PFOS/PFOA LC/MS/MS conditions (example)

LC conditions

Instrument	: LC-MS/MS
column	: Inersil ODS-SP (15 cm×2.1 mm ID、3 μm) GL Science
phase A	: 10 mM Ammonium acetate
phase B	: Acetonitrile
gradient	: 0-1min A : 65% B : 35% 1-5min A : 65→50% B : 35→50% 5-15min A : 50% B : 50% 15-18 min A : 50→10% B : 50→90% 18-25 min A : 10% B : 90% 25-25.1 min A : 10→65% B : 90→35% 25.1-35 min A : 65% B : 35%

Flow rate : 0.2 mL/min

Col. Temp. : 40 °C

Inj. volume : 10 μL

MS conditions

Instrument	: API 3200 (Applied Biosystems)
Ionization	: ESI negative
Monitor ions (<i>m/z</i>)	: PFOS 498.7→79.9 (quant.) 498.7→98.9 (confirm.) PFOA 412.7→368.8 (quant.) 412.7→169.0 (confirm.) ¹³ C ₄ -PFOS 502.9→79.9 ¹³ C ₄ -PFOA 416.9→372.0

PFOS	Wellington Laboratories
PFOA	Wellington Laboratories
¹³ C ₄ -PFOS	Wellington Laboratories
¹³ C ₄ -PFOA	Wellington Laboratories

PFOS and related substances and PFCs – instrumental approach and masses

Table A2-6: PFOS, PFOS related substances and other PFCs included in state-of-the-art monitoring.
Please note: Red marked substances are PFOS and related substances.

Abbreviation	Full name	CAS #	Detection method
Fluorooctane sulfonamides/ sulfonamidoethanols			
PFOSA*	Perfluorooctane sulfonamide	754-91-6	LC-MS
N-Me-FOSA*	N-Methyl-heptadecafluorooctane sulfonamide	31506-32-8	LC-MS
N-Et-FOSA	N-Ethyl-heptadecafluorooctane sulfonamide	4151-50-2	LC-MS
N-Me-FOSE*	N-Methyl-heptadecafluorooctane sulfonamidoethanol	24448-09-7	LC-MS
N-Et-FOSE*	N-Ethyl-heptadecafluorooctane sulfonamidoethanol	1691-99-2	LC-MS
Fluortelomer alcohols			
4:2 FTOH	4:2 Fluorotelomer alcohol	2043-47-2	GC-MS or LC-MS
6:2 FTOH	6:2 Fluorotelomer alcohol	647-42-7	GC-MS or LC-MS
8:2 FTOH	8:2 Fluorotelomer alcohol	678-39-7	GC-MS or LC-MS
10:2 FTOH	10:2 Fluorotelomer alcohol	865-86-1	GC-MS or LC-MS
Fluortelomer sulfonates			
6:2 FTS	6:2 Fluorotelomer sulfonate	27619-97-2	LC-MS
8:2 FTS	8:2 Fluorotelomer sulfonate	39108-34-4	LC-MS
Fluortelomer carboxylates			
6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylate	C ₈ H ₂ F ₁₂ O ₂ *	LC-MS
8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylate	70887-84-2	LC-MS
Perfluoro sulfonates			
PFBS	Perfluorobutane sulfonate	375-73-5	LC-MS
PFHxS	Perfluorohexane sulfonate	432-50-7	LC-MS
PFOS*	Perfluorooctane sulfonate	1763-23-1	LC-MS
PFDCS	Perfluorodecane sulfonate	335-77-3	LC-MS
Perfluoro carboxylates			
PFBA	Perfluorobutanoate	375-22-4	LC-MS
PFPA	Perfluoropentanoate	2706-90-3	LC-MS
PFHxA	Perfluorohexanoate	307-24-4	LC-MS
PFHpA	Perfluoroheptanoate	375-85-9	LC-MS

PFOA	Perfluorooctanoate	335-67-1	LC-MS
PFNA	Perfluorononanoate	375-95-1	LC-MS
PFDcA	Perfluorodecanoate	335-76-2	LC-MS
PFUnA	Perfluoroundecanoate	2058-94-8	LC-MS
PFDcA	Perfluorododecanoate	307-55-1	LC-MS
PFTTrA	Perfluorotetradecanoate	376-06-7	LC-MS
Polyfluoro alkyl phosphate esters (PAPs)			
4:2 monoPAPs	4:2 mono alkylated phosphate ester		LC-MS
6:2 monoPAPs	6:2 mono alkylated phosphate ester		LC-MS
8:2 monoPAPs	8:2 mono alkylated phosphate ester		LC-MS
10:2 monoPAPs	10:2 mono alkylated phosphate ester		LC-MS
4:2/4:2 diPAPs	4:2/4:2 dialkylated mercapto ether phosphate diester		LC-MS
4:2/6:2 diPAPs	4:2/6:2 dialkylated mercapto ether phosphate diester		LC-MS
6:2/6:2 diPAPs	6:2/6:2 dialkylated phosphate diester		LC-MS
6:2/8:2 diPAPs	6:2/8:2 dialkylated phosphate diester		LC-MS
8:2/8:2 diPAPs	8:2/8:2 dialkylated phosphate diester		LC-MS
8:2/10:2 diPAPs	8:2/10:2 dialkylated phosphate diester		LC-MS
10:2/10:2 diPAPs	10:2/10:2 dialkylated phosphate diester		LC-MS
10:2/12:2 diPAPs	10:2/12:2 dialkylated phosphate diester		LC-MS
12:2/12:2 diPAPs	12:2/12:2 dialkylated phosphate diester		LC-MS
Fluorotelomer Mercapto alkyl phosphate diesters FTMAPs (S-diPAPs)			
6:2/6:2 FTMAPs	6:2/6:2 dialkylated mercapto ether phosphate diester		LC-MS
6:2/8:2 FTMAPs	6:2/8:2 dialkylated mercapto ether phosphate diester		LC-MS
8:2/8:2 FTMAPs	8:2/8:2 dialkylated mercapto ether phosphate diester		LC-MS
8:2/10:2 FTMAPs	8:2/10:2 dialkylated mercapto ether phosphate diester		LC-MS
10:2/10:2 FTMAPs	10:2/10:2 dialkylated mercapto ether phosphate diester		LC-MS
10:2/12:2 FTMAPs	10:2/12:2 dialkylated mercapto ether phosphate diester		LC-MS
12:2/12:2 FTMAPs	12:2/12:2 dialkylated mercapto ether phosphate diester		LC-MS

*No CAS number available

PFOS LC/MS/MS chromatogram

PFOS標準品 0.5 ng/mL

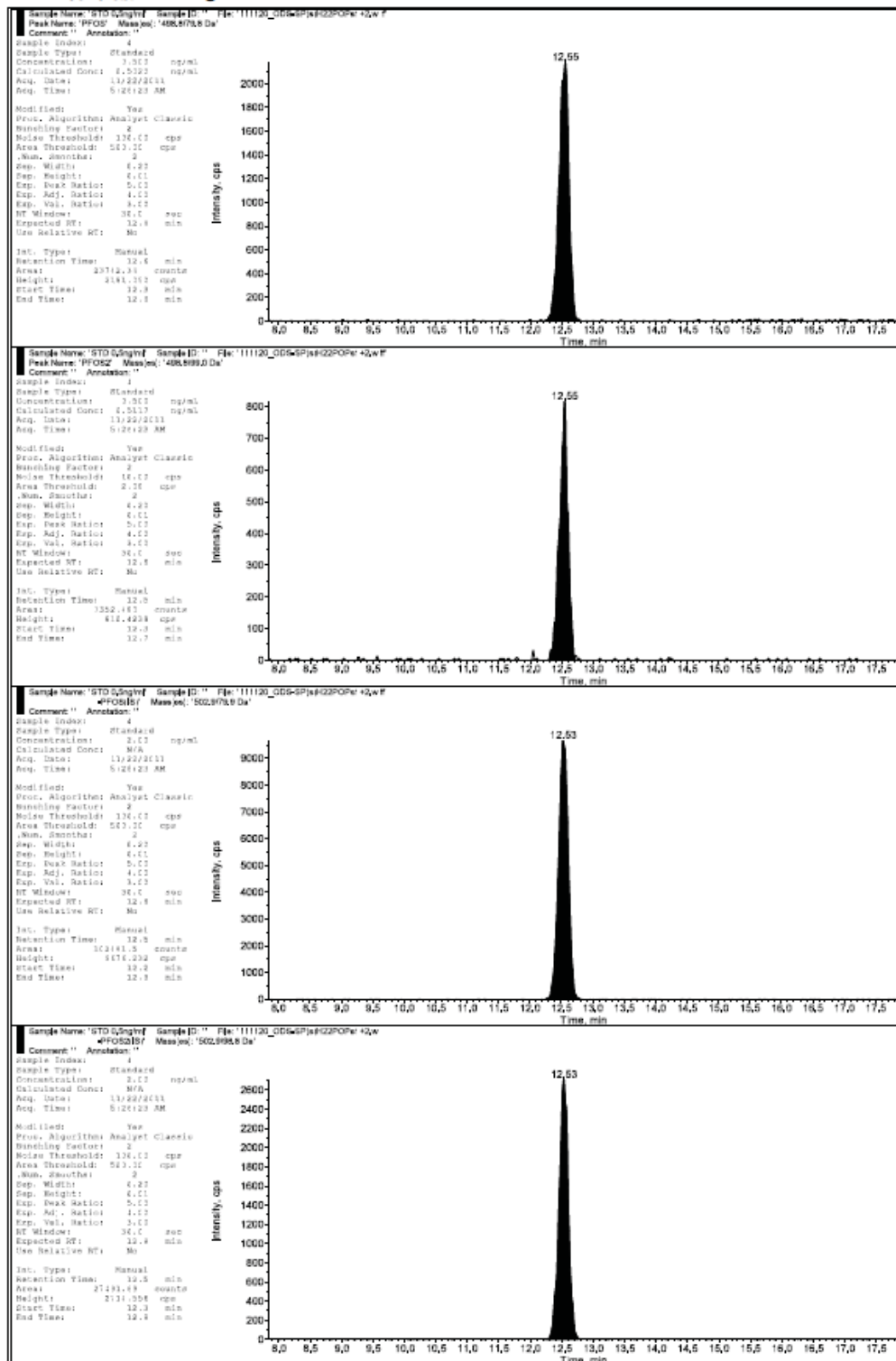


Figure A2-9: Chromatogram of PFOS on Inersil ODS-SP column.

Annex 2-E: LC/MS analysis of Chlordecone

Chlordecone LC/MS/MS conditions (example)

LC Conditions

Instrument	:	LC-MS/MS
Column	:	Develosil C30-UG-5 (15 cm×2.0 mmID、5 μm) Nomura chemical
phase A	:	Water
phase B	:	Methanol
gradient	:	0-3 min A : 40% B : 60% 3-7 min A : 40→0% B : 60→100% 7-19 min A : 0% B : 100% 19-26 min A : 40% B : 60%
Flow rate	:	0.2 mL/min
Col. temp.	:	40 °C
Inj. volume	:	10 μL

MS Conditions

Instrument	:	API 4000(Applied Biosystems)
ionization	:	ESI negative
Monitor ions (<i>m/z</i>)	:	Chlordecone 506.7→426.5 (quant.) 508.7→428.8 (confirm) ¹³ C ₁₀ -Chlordecone 516.8→435.7

Chlordecone	Cambridge Isotope Laboratories
¹³ C ₁₀ - Chlordecone	Cambridge Isotope Laboratories

Chlordecone LC/MS/MS chromatogram

Chlordecone標準品 0.01 ng/mL

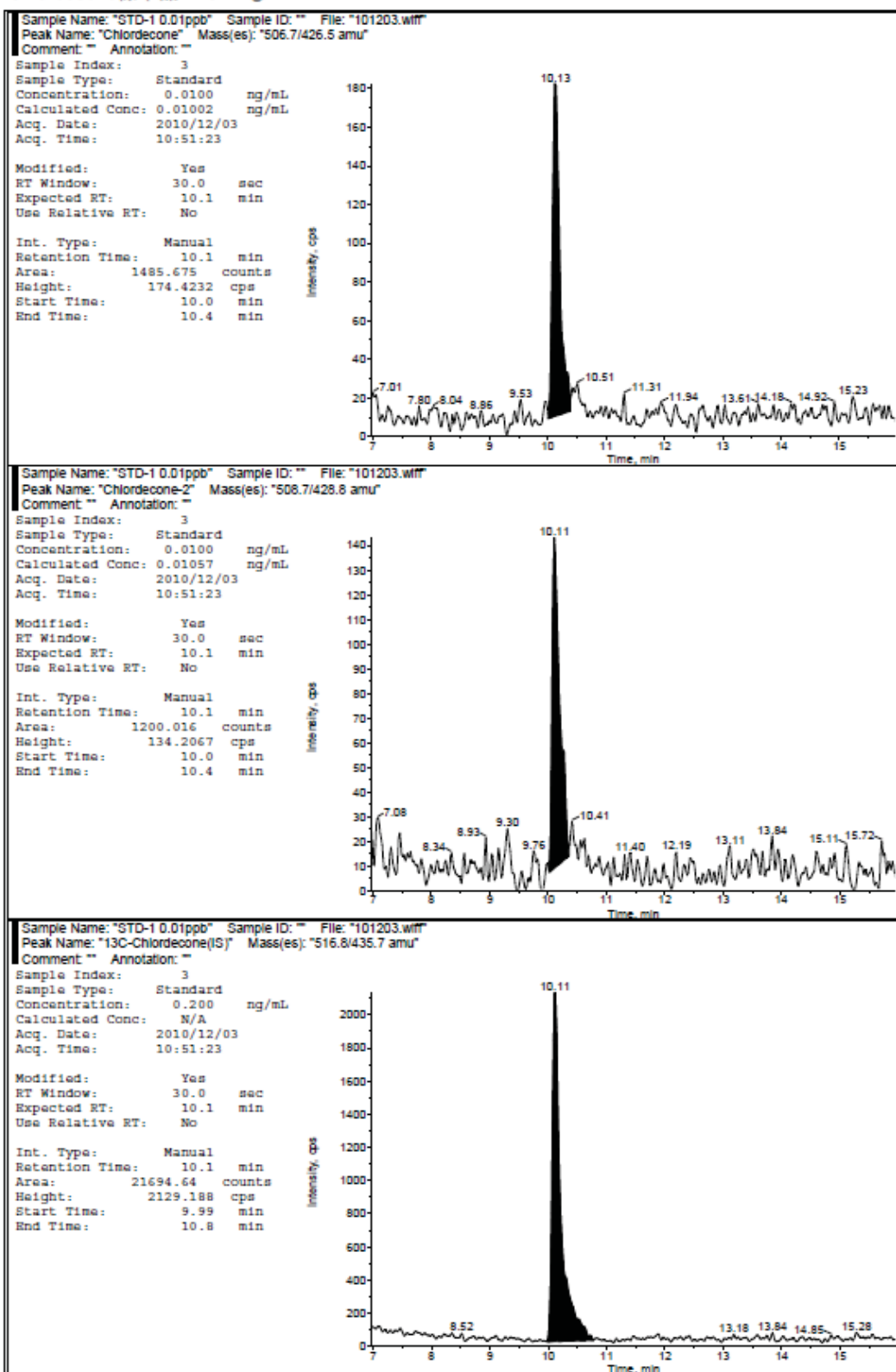


Figure A2-10: Chromatogram of Chlordecone on Develosil C30-UG-5 column.

ANNEX 3 Case studies

Case studies of PFOS¹⁰⁵/PFC screening in products, articles and wastes

Monitoring project of PFOS/PFCs in consumer products in Norway and Sweden

The Norwegian Pollution Control Authority (SFT) has commissioned a survey carried out by Swerea IVF (Sweden) together with Norwegian Institute for Air Research (NILU) that aimed to identify and quantify possible sources of PFC in Norway in industrial manufacturing and applications used by the Norwegian population in daily life (Herzke et al. 2009)¹⁰⁶

The study included waterproofing agents (5), paint and inks (5), impregnated products: paper, textiles, leather and carpets (2/2/2/2), non stick ware (6), electronics (5) and fire fighting agents (5).

PFOS, which has been banned in Norway since 2007, was detected in 47% of samples in low concentrations and only in 4 of the 34 analysed products the amounts were close to or exceeding the regulation.¹⁰⁷ These products were all within the leather or carpet product groups: The two leather samples had the highest concentrations of PFCs: Office furniture leather; (pool of 3) and black shoe, leather, showed PFOS levels of 38 and 21 $\mu\text{g}/\text{m}^2$, exceeding the EU regulation of 1 $\mu\text{g}/\text{m}^2$. Carpets were around the regulation of 1 $\mu\text{g}/\text{m}^2$. The relatively low levels detected indicate that PFOS were not applied as major performance chemical but rather as by-product or contaminant of other PFCs or treatment procedure. Only five of the 34 analysed industrial materials and consumer products contained none of the analysed 29 polyfluorinated substances.

Specific feature of the Norwegian study on screening PFOS/PFCs in consumer products:

- Sample candidates were identified in different ways:
 - by having or giving certain properties that are common for perfluorinated chemicals (e.g water repellent, stain resistant, anti-grease, non-stick, surfactant), by their previous known high concentration of PFCs (Teflon table cloth, AFFF, water proofing agents) or
 - by information from literature that production of these articles may include perfluorinated chemicals (epoxy resin board, semiconductor fabrication etc.).

A number of product types were identified as potential PFC containing groups and several samples were collected in each group distributed as

- Good analytical coverage: 29 different PFCs were analysed in all collected samples
- Regional approach: Cooperation of Norway and Sweden.
- Data published in a report in the public domain with product names

¹⁰⁵ The USEPA (2009) did a monitoring study on "[Perfluorocarboxylic Acid Content in 116 Articles of Commerce](#)". Since the study did not monitor for PFOS it is not described here.

¹⁰⁶ Herzke D, Posner S, Olsson E (2009) Survey, screening and analyses of PFCs in consumer products. TA-2578/2009; Swerea IVF Project report 09/47. <http://www.klif.no/publikasjoner/2578/ta2578.pdf>

¹⁰⁷ Regulation EC No 552/2009 of 22 June 2009 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XVII, p.53.

Case study Baking and Muffin papers (Schlummer et al. 2011)¹⁰⁸

As a contribution to the European Perfood project (<http://www.perfood.eu/>; KBBE-227525), 154 paper-based food contact materials were collected and screened for fluorinated contaminants. As screening methods sliding spark spectroscopy, wave length dispersive x-ray fluorescence and DART-MS were applied. 47 fluorine-positive samples were identified and subjected to a detailed analysis for PFOS and other perfluorinated sulfonates (PFSA), fluorotelomer alcohols (FTOH), and perfluorinated carboxylates (PFCA). Samples were fortified with isotope-labelled standards of PFSA, FTOH, and PFCA, and extracted with methanol by pressurized liquid extraction (PLE, ASE 200, Dionex, Germany). In order to avoid cross contaminations, the PLE apparatus was equipped with Teflon-free tubes and carefully checked for blanks. The methanol extracts were split into two equal aliquots. One aliquot was subjected to GC-(CI)-MS (TSQ 7000, Thermo) analysis using methane for chemical ionisation. The other aliquot was cleaned by SPE (Oasis WAX) and measured by LC-(ESI)-MS/MS (LC Quattro, Waters). For both analytical approaches quantification was based on an isotope dilution method.

In this study, PFOS and other perfluorinated sulfonates (PFSA) were not detected in any sample at levels above 1 ng/g. Instead 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were identified in all fluorine positive samples at levels ranging from 9 to 39500 ng/g, whereas 4:2 FTOH were only quantified in about 25% of the samples (maximum value 54 ng/g). Concentrations of PFCA were considerably lower and ranged from LOD (<1) to 619 ng/g PFOA, LOD (<1) to 1500 ng/g PFNA, and LOD (<1) to 390 ng/g PFDA.

This strongly indicates a switch from FOSE-based coatings for paper to FTOH containing macromolecules in industrial practise. Three patterns of PFCA congeners could be distinguished and may indicate to at least three different mother compounds, i.e. fluorine based paper coatings:

Pattern A: dominated by more or less equal amounts of PFOA, PFDA and Perfluorododecanoic acid (PFDoA),

Pattern B: dominated by PFOA and PFNA followed by PFHpA and PFDA.

Pattern C: clearly dominated by PFHxA.

In this first screening studies performed in 2009/2010, most baking and muffin papers were fluorine positive and had significant FTOH and PFCA levels. However, in a second screening in 2010/11 a series of baking and muffin papers were re-analysed. And this time, most samples were fluorine negative in the screening (detection limit approx. 0.1%), meaning that most of the investigated brand marks had changed for the European market their coating in recent years towards non-organofluorine coatings and already some years before have moved away from PFOS precursor based coatings.

Monitoring of paper packaging for food (Denmark)¹⁰⁹

PFOS and related chemicals in food packaging are of particular concern due to possible direct human exposure. In an (on-going) survey for the Danish Food Administration approximately 85 samples were taken by food inspectors in food packaging businesses (samples with no previous contact with food) and by DTU-Food in retail stores (samples in contact with foods). Three subsamples of 0.2 dm² each were combined in 60 ml 50% ethanol/water and extracted for 24 hrs at 60 °C. The extracts/migrates were filtered through 0.2 µm nylon/PP filters and analysed by an UHPLC-ESI⁻-MS/MS (Waters Quattro Ultima) method in single reaction monitoring (SRM also called SIR) mode for the compounds listed in Table XX. An Acquity C₁₈ CSH column (1.7 µm*2.1 mm*150

¹⁰⁸Schlummer M, Gruber L, Fengler R, Fiedler D, Wolz G (2011) How Poly- And Perfluoroalkyl Substances (PFAS) May Enter Our Food From Food Contact Materials (FCM). [Perfood Newsletter, Issue 2](#): November 2011

¹⁰⁹ Danish Veterinary and Food Administration (2012) Danish Technical University Report (not published).

mm, Waters) was used with a 35 min gradient program, with MeOH/water (+NH₄OH) mobile phase, Trier 2011 - JCA).

In the SIR mode only the deprotonated precursor ion was transmitted, in order to maintain high enough sensitivity while analysing for many compound on this instrument, which only has 20 Hz data sampling frequency. In the MRM methods two MRM transitions were used, but the method was then split up into three separate methods to maintain a high enough sensitivity of particularly the polyfluorinated compounds (FTOHs, PAPs): 1) Even PFCAs+PFSAs+PFOSA+FTMAPs, 2) Un-even PFCAs+FTOHs, 3) monoPAPs and diPAPs. ¹³C internal standards included 6:2, 8:2 monoPAPs, and 6:2/6:2, 8:2/8:2 diPAPs, 8H-7:1 FTOH and 9H-PFNA. The internal standard corrected well, except for very water soluble PFCs, possibly due to ion suppression by co-eluting salts. The previous d₄-6:2/6:2 diPAPs was found to contain considerable amounts of d₂-6:2 monoPAPs, formed either by hydrolysis from storage in water/alcohol or from impurities. Consequently the monoPAPs and diPAPs standards were not mixed. Loss of analytes was a big problem, and working solution only kept for < 1 week. Only four samples contained PFSAs, and only two of these contained PFOS but in low levels (< 10 ppb). The other samples contained FTOH based PFCs in 57 % of the samples. However by an MRM method, the early eluting ions of 4:2 monoPAPs and PFBA were found to have interferences from the matrix. The study confirmed a previous study from the Danish, Canadian and Swedish markets sampled in 2009, where fluorinated compounds were present in 60% of the paper and board samples (Trier 2011), but the levels in the samples from 2010-2011 had generally decreased. Also this study revealed/conformed with the pattern of detected PFCs that industry already have shifted away from PFOS-derived coatings to diPAPs and now towards FTOH containing coatings. PFCA impurities/breakdown products were often seen in the paper extracts/migrates.

Non-analytical screening of PFOS/PFCs on the Danish market (Danish Ministry of Environment 2008)

In the first steps of monitoring of newly listed POPs in a country other approaches (including import statistics, product registers, company survey and audits than instrumental screening and analysis should be considered and used (for details please see the "*Strengthening POPs Regulatory Framework Guidance*"¹¹⁰). One documented survey in this respect has been published for Denmark¹¹⁰. The main purpose of this project was to estimate the use of PFOS and other PFCs in consumer products in Denmark.

Approaches of the Danish market survey of PFOS/PFCs on the national market were:

- Compilation of information from the Danish Product Register.
- Information from different companies such as producers, importers, suppliers and stores. Producers of fluorinated substances have been identified by Internet survey.
- The most important companies within the most relevant sectors were contacted by phone (not by questionnaires). This approach only gave sparse information (either companies did not know the chemical content of their products or they did not want to give information about the use of fluorinated substances (the survey was performed by a consultancy and not by a competent authority).
- Stores and companies marketing and selling consumer products with a content of fluorinated substances have been identified initially by identifying the different products that contain fluorinated substances, and then secondly identifying the sectors in which the products are sold or produced.

¹¹⁰ Danish Ministry of Environment (2008) Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, No. 99, 2008.

- Information found on the Internet search about the content of fluorinated substances in different products was combined with statistics of sales of products in Denmark in order to estimate the use of fluorinated substances in Denmark in different product categories.

DRAFT

Case studies of PBDE screening in products, articles and wastes

A few countries/institutes or NGOs have performed screening of PBDE in articles and wastes. These case studies already give a good insight into POP-PBDE contamination of several material/recycling flows. The case studies are shortly described below with links to the reports/publications mentioned in footnote with respective web-link.

Monitoring of PBDEs in WEEE plastic in EU (Wäger et al. 2010)¹¹¹

The largest and most relevant substance flow of POP-PBDEs and BFR containing materials are plastic fractions from WEEE recycling. The Swiss national material testing institute EMPA developed a standardized methodology for sampling of WEEE plastic (Annex 4-A and Annex 4-B) for a survey of RoHS regulated substances in WEEE plastic in Europe including c-OctaBDE. The report on the study can be downloaded at EMPA's E-waste (WEEE) information Web-page (<http://ewasteguide.info/>¹¹²; containing additionally a wide range of overview articles on all E-waste related issue).

Specific features of EMPA's case study on PBDE and other RoHS relevant substance screening in WEEE plastics are:

- In the study a sampling methodology and a sampling protocol has been developed and is described in detail of [Annex 1 and Annex 2 of EMPA study](#). This sampling strategy and protocol can be applied (in a modified way) in other countries and regions having shredder plants for processing of WEEE.
- The study gives a broad overview on the current POP-PBDE content of the polymer fractions of WEEE categories in Europe.
- The study further gives an overview on other critical RoHS relevant pollutants which might be relevant today for other regions too.

Determination of POPs-PBDE and BFRs in WEEE plastics in Nigeria ([Sindikü et al. 2011](#)¹¹³ and [2012](#)¹¹⁴)

The largest POP-PBDE share within EEE/WEEE are casings of Cathod Ray Tubes (CRTs) (see *PBDE Inventory Guidance*³). In a monitoring study of POP-PBDEs in Nigeria the two major CRT categories (TVs and computers) were monitored ([Sindikü et al. 2011](#) and [2012](#)). In this case study 383 single housings of computer and TV Cathode Ray Tubes (CRTs) were sampled at WEEE storage sites in Nigeria (Sindikü et al. 2011, 2012). Furthermore the recycling of the plastic (large share is ABS) of these appliances is of particular interest from an economic perspective.

383 single housings of computer and TV Cathode Ray Tubes (CRTs) were sampled at WEEE storage sites in Nigeria (Sindikü et al. 2011, 2012). These two electronic appliances contain the largest share of POP-PBDEs in EEE/WEEE (POP-PBDE Inventory Guidance). Furthermore the recycling of the plastic (large share is ABS) of these appliances is of particular interest from an economic perspective.

¹¹¹ Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. [Final Report September 17, 2010](#).

¹¹² Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. [Final Report September 17, 2010](#).

¹¹³ Sindikü et al. (2011) Screening E-waste plastic in Nigeria for BFR using XRF – towards a methodology for assessing POPs PBDE in Ewaste exports. [Organohalogen Compounds 73. 785-788](#).

¹¹⁴ Sindikü O, Babayemi JO, Osibanjo O, Schlummer M, Schluep M, Weber R (2012) Assessing POP-PBDEs and BFRs in E-waste polymers in Nigeria. [Organohalogen Compounds 74, 1320-1323](#).

The samples were specifically selected from waste storages, electronics workshops, roadsides, dumpsites and dismantling sites. The labels on the TVs and computer monitor plastic housings were examined for information on the manufacturer, brand, model, serial number, year and origin of production. Mainly for TV samples, the year of production were found printed on the inside of the plastic casings. The information was immediately recorded and about 250 cm² sizes were cut from each sample. Dismantling and cutting were done with simple tools (Figure A4-1). A hole was made on the cut samples through which a metal tag (Figure A4-2) was attached with the aid of a safety pin (Figure A4-3). These were transferred to the workshop where 40 mm X 40 mm squares were cut (Figure A4-4), and the cut squares packaged in labelled drug envelopes (Figure A4-5) for further analytical screening and analysis and stored for further analysis at a dark place, in order to avoid degradation processes.

The ranges of the year of production were 1987-2006 for computers, and 1981-2004 for TVs. This time span is considered being the most relevant for the use of POP-PBDEs as their use is thought to have been stopped in about 2004.

The numbers of samples with the regions of origin (production or assembly) are shown in Table A-3. A total of 382 samples were collected - 224 Computers and 158 TV sets. For computer samples, the highest proportion originated from Asia (100), followed by America (74), and then Europe (50). Most of the TV samples were produced in Europe (100), followed by Asia (58), and none from America. This broadly reflects presence of these e-wastes in Nigeria. Second hand TVs are not imported from the US as the systems are not compatible.



Figure A4-1: Sampling tools

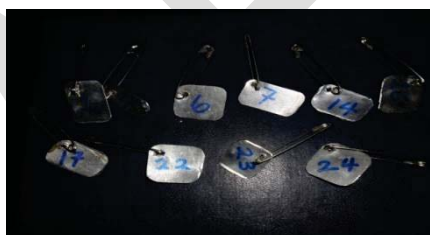


Figure A4-2: Labelling tags



Fig. A4-3: Labeled field sample



Figure A4-4: Cut squares



Figure A4-5: packaged samples

Table A4-1: Number of samples from each region of production/assembly

Region	Computer	TVs	Total
Europe	50	100	150
Asia	100	58	158
America	74	0	74
Total	224	158	382

Small parts of these sub-samples were subjected to a screening with EDXRGF aiming at the semi-quantification of bromine, chlorine but also of inorganic compounds listed in the RoHS directive. Bromine positive samples were then selected for GC/ECD and GC/MS analysis.

Extraction was performed by a dissolution/precipitation approach, since most casings were built by styrene based polymers which at least partly dissolve in classic extraction solvents (e.g. acetone, acetone/cyclohexane, ethyl acetate, THF, toluene, etc.). Dissolution was performed by THF and precipitation by *n*-heptane (see methodology described above).

In case of high bromine levels, GC-ECD provides typical fingerprint of technically applied BFRs. However, in case of lower bromine concentrations (below 1000 ppm) and unclear ECD results the aliquots of the sample extracts were fortified with ¹³C-labelled internal standards and further subjected to GC/MS analysis in the EI-mode. By this approach an emission factor for octaBDE in the two key (TV casings and computer monitors) were derived.

Finally, the type and amount of BFR have been measured for 382 computers and products.

Specific features of the case study on BFR screening and PBDE in WEEE plastic are:

- In the study a sampling methodology of CRT polymers for countries having no shredder plants (and where the above mentioned EMPA approach is difficult to apply) have been developed and are described in Annex 4-C.
- Bromine screening was applied and POP-PBDE content separately for the different main importing regions (North America, Asia, and Europe).
- Product specific information (producer, product name, production year, region of origin) on POP-PBDE/BFR content in the CRTs products specific.
- With the generated data set POP-PBDE impact factors for plastic of TV CRTs (6.9 kg c-OctaBDE/tonne TV CRT plastic) and computer CRTs (0.5 kg c-OctaBDE/tonne PC CRT plastic) in Nigerian. Based on the EEE/WEEE inventory of Nigeria¹¹⁵ these impact factors have been used for developing the POP-PBDE inventory for Nigerian EEE/WEEE.

The EDC chromatogram in Figure 2 b and c show BFRs mixtures in polymers from two TV samples containing c-OctaBDE. The mixtures of BFR reveal that the casings of the two TV sets were produced partly with recycled polymers.

Monitoring of BFRs in polymers of electronics on Swiss market (Bantelmann et al. 2010)¹¹⁶

The Swiss competent authorities monitored in 2000 consumer products the presence of brominated flame retardants including electrical devices, building materials and lighting equipment. The aim of the survey was to evaluate the compliance of commercial articles with the provisions of the Swiss restrictions on BFRs: In Switzerland, the placing on the market and use of PBBs, c-PentaBDE, and c-OctaBDE as substances on its own, as well as in preparations with contents of each of these BFRs equal to or exceeding 0.1% by mass is prohibited. Placing on the market – but not the use – of articles that contain these substances in concentrations equal to or exceeding 0.1% by mass is banned as well.

Only 2 from the approximately 2000 samples contained c-OctaBDE above the 0.1% RoHS threshold.

Specific features of the case study on PBDE and other RoHS relevant substances in WEEE plastic are:

- The study is a comprehensive market survey with a three step approach to monitor brominated flame retardants in contemporary products

¹¹⁵ Ogungbuyi O, Nnorom IC, Osibanjo O, Schluep M (2012) Nigeria e-Waste Country Assessment. Basel Convention Coordinating Centre for Africa (BCCC-Nigeria) and Swiss EMPA, Ibadan, Nigeria and St.Gallen, Switzerland May 2012.

¹¹⁶ Bantelmann E, Ammann A, Näf U, Tremp J. (2010) Brominated flame retardants in products: Results of the Swiss market survey 2008. BFR 2010, April 7-9, Kyoto, Japan <http://www.bfr2010.com/abstract-download/2010/90004.pdf>.

- Screening of BFRs in products
- Analysis of the bromine positive samples for prohibited POP-PBDEs and common used flame retardants
- Scanning of bromine positive samples where the BFR were not those commonly used for new brominated flame (Zennegg et al. 2011)¹¹⁷
- The study gives an insight on BFRs used in electronic products imported to the European market. The study shows that the POP-PBDE content in current products on the Swiss (and therefore European) market is small.
 - Only 2 from the approximately 2000 samples contained c-OctaBDE above the 0.1% RoHS threshold.
 - 17 samples contained DecaBDE above the RoHS threshold of 0.1%
- The study further gives an overview on other critical RoHS relevant pollutants which is relevant today for many other regions with RoHS like legislation

The results of the third screening level of unknown BFRs in the samples by EMPA revealed that some of these samples contained e.g. hexabromobenzene or pentabromobenzene where the chlorinated analogues (HCB & PeCB) are prohibited by the Stockholm Convention.

Monitoring POP-PBDEs in carpet rebond from recycled PUR foam ([DiGangi et al. 2011](#))¹¹⁸

PUR foam is recycled to carpet rebond in some regions in particular North America (see Guidelines on BAT and BEP for the recycling and waste disposal of articles containing PBDEs listed under the Stockholm Convention).

Recently, a [monitoring project](#) of POP-PBDEs in carpet rebond was performed with XRF for bromine screening and 26 samples were analysed for PBDE by GC/MS analysis.

Specific features of the case study on PBDE and screening of carpet rebond:

- The study combines bromine screening methodology with confirmation analysis (as suggested in this guidance document)
- The study sampled in different world regions covering industrial and developing countries.
- The study addresses a product category manufactured from recycling materials possibly impacted by POP-PBDE-containing materials
- The study was planned and performed from an NGO working on POPs (www.IPEN.org) and results were published including the company names with high/low impacted products that consumers could assess company performance and possibly ask a company when purchasing similar products

¹¹⁷ Zennegg M (2011) Identification of "Novel" Brominated flame retardants in new products of the Swiss market. [Organohalogen Compounds 73, 1238-1241](#).

¹¹⁸ DiGangi J, Strakova J, Watson A (2011) A Survey of PBDES in Recycled Carpet Padding. [Organohalogen Compounds 73, 2067-2070](#).

Monitoring of POP-PBDEs and other flame retardants in baby products [\(Stapleton et al. 2011\)](#)¹¹⁹

PUR foam samples collected from 101 commonly used US baby products were monitored for POP-PBDEs and other flame retardants [\(Stapleton et al. 2011\)](#). From these products:

- Five samples contained POP-PBDE congeners commonly associated with c-PentaBDE, suggesting that such products are still in-use in sensitive use areas although production of c-PentaBDE is considered to have stopped in 2004¹²⁰.
- 80% of the PUR foam baby products contained an identifiable flame retardant additive, and all but one of these was either chlorinated or brominated compounds.
- The most common flame retardant detected was tris(1,3-dichloroisopropyl) phosphate (TDCPP; detection frequency 36%), followed by polybrominated aromatic compounds typically found in the Firemaster550 commercial mixture (detection frequency 17%).

Specific features of the case study on BFR/PBDE and CFR screening in PUR baby products:

- The study combined bromine screening methodology with confirmation analysis (as suggested in this guidance document). A portable X-ray fluorescence (XRF) analyser was used to estimate the bromine and chlorine content of the foams. A significant correlation was observed for bromine with quantitative analysis of BFRs; however, there was no significant relationship observed for chlorine and CFRs.
- For the first time a wide range of polyurethane baby products were sampled, screened and analysed for POP-PBDEs and other flame retardants.
- Based on exposure estimates conducted by the US Consumer Product Safety Commission, the study predict that infants may receive greater exposure to TDCPP from these products compared to the average child or adult from upholstered furniture, all of which are higher than acceptable daily intake levels of TDCPP set by the US Consumer Product Safety Commission.
- The study revealed that flammability standard¹²¹ in a country can result in high levels of flame retardant in sensitive products with critical exposure to vulnerable groups like infants.

Monitoring of POP-PBDE in children toys

A Chinese research group assessed the presence of PBDEs and other BFRs (including PBBs, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE)) in children's toys purchased from South China (Chen et al. 2009)¹²². In all samples PBDE or other BFRs were detected. The median BFR concentrations in the hard plastic toys were notably higher than values in other toys. The PBDE concentrations were below the threshold limit (1000 ppm) required by the European Commission's Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) directives in all of the toys, except for one hard plastic toy with a total PBDE concentration of 5344 ppm. The BFR profiles in the toys were consistent with the patterns of

¹¹⁹ Stapleton MH, Klosterhaus S, Keller A, Ferguson PL, van Bergen S, Cooper E, Webster TF, Blum A (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. [Env. Sci. Technol. 45. 5323-5331.](#)

¹²⁰ With some uncertainties for the c-PentaBDE production in China which might have stopped later.

¹²¹ Baby products containing PUR foam must meet California state furniture flammability standards, which likely affects the use of flame retardants in baby products throughout the U.S and possibly North America.

¹²² Chen S-J, Ma Y-J, Wang J, Chen D, Luo X-J, Mai B-X (2009) Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure & Risk Assessment. *Environ Sci Technol* 43, 4200- 4206.

their current production and consumption in China, where PBDEs, specifically decaBDE product, were the dominant BFR, followed by the emerging DBDPE. The relatively high concentrations of octa- and nonaBDEs in the foam toys may suggest the decomposition of highly brominated BDEs during the manufacturing processes of the toys.

Specific feature of the study analysing POP-PBDEs and other BFRs in toys:

- This was the first study to examine the concentrations of PBDEs and other BFRs in toys, and the potential exposures to children.
- Revealed the broad use of recycled WEEE plastic in sensitive use areas like children toys.
- The study highlighted that because of extended periods of play, mouthing behaviour, and frequent hand-to-mouth contact, toys may pose a significant pathway of BFR exposure in children.
- Together with a second study of the group on PBDE/BFR screening in household goods¹²³, the research reveals that the recycling of WEEE plastics seems largely uncontrolled in some regions.

¹²³Chen S-J, Ma Y-J, Wang J, Tian M, Luo X-J, Chen D, Mai B-X (2010) Measurement and human exposure assessment of brominated flame retardants in household products from South China. *J. Hazard. Mater.* 176, 979-984.

Case studies of PeCBz, HCB and PCDD/PCDF in articles and products

Screening of unintentionally POPs in chloranil (Liu et al. 2012¹²⁴)

Unintentionally POPs including PeCBz, HCB and PCDD/PCDF has recently been screened in chloranil samples from Chinese producers. Extremely high levels of PCDD/PCDF (522 µg TEQ/kg) were detected in one chloranil product and therefore with PCDD/PCDF levels 35 times above the low POPs threshold (15 µg TEQ/kg) of the Basel Convention for wastes. The estimated total PCDD/PCDF content of this currently marketed chemical from China alone was 1044 g TEQ, which is about 10% of China's total PCDD/PCDF inventory, but present directly in treated consumer products. PeCBz, HCB, and PCB were also detected in these chemicals in relevant concentrations (Liu et al., 2011).

Monitoring of HCB in ([Government of Japan 2006](#)¹²⁵ and [2007](#)¹²⁶)

The Japanese government have submitted two reports on HCB in Tetrachlorophthalic acid (TCPA, tetrachloro-1,2-benzenedicarboxylic acid)¹²⁷ and related pigments (e.g. Pigment Yellow 110 (CAS Registry Number 5590-18-1), Pigment Yellow 138 (CAS Registry Number 30125-47-4), Solvent Red 135; Solvent Red 162; (CAS Registry Number 20749-68-2 and 71902-17-5)) to the COP4 ([Government of Japan 2006](#) and [2007](#)). These case studies can be seen from product coverage as state of art approach of monitoring unintentionally POPs in products. The limitation of the study is that no PeCBz or PCDD/PCDF has been reported. Unintentionally HCB levels for TCPA were found up to 3,000 ppm ([Government of Japan 2006](#)) and the suggested BAT levels for TCPA and pigments were in ppm range (up to 200 ppm).

Specific features of the reports

- Comprehensive dataset on HCB in TCPA and key related pigments
- Background information on production processes and cleaning steps for the products and related achievable HCB levels
- Suggestion on BAT approach for minimizing HCB with suggested BAT/BEP levels

Monitoring of pesticides for unintentionally POPs ([Huang et al. 2012](#)¹²⁸, [Holt et al. 2010](#)¹²⁹)

In a Chinese study five pentachloronitrobenzene (PCNB) pesticide products (including 2 raw pesticide products and 3 formulations) were analysed for unintentionally POPs including HCB, PeCBz, PCB and PCDD/PCDF. All investigated unintentionally POPs were detected in all formulations. For some formulation the TEQ contribution from PCB were higher compared to total PCDD/PCDF TEQ contribution.

¹²⁴ Liu W, Tao F, Zhang W, Li S, Zheng M, (2012) Contamination and emission factors of PCDD/Fs, unintentional PCBs, HxCBz, PeCBz and polychlorophenols in chloranil in China. *Chemosphere* 86, 248-251.

¹²⁵ Government of Japan (2006) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in TCPA and Solvent Red 135. November 2006.

¹²⁶ Government of Japan (2007) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in Other Pigments Derived from TCPA and Phthalocyanine.

¹²⁷ The dimethyl ester of tetrachlorophthalic acid is used as an herbicide, Dacthal.

¹²⁸ Huang J, Yu G, Deng S, Wang B, Wu C, Yamazaki N, Weber R (2012) Determination of PCDD/Fs and dl-PCBs as impurities in Chinese pentachloronitrobenzene pesticides. *Organohalogen Compds* 74, 1429-1432.

¹²⁹ Holt E, Weber R, Stevenson G, Gaus C (2010) Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/Fs) Impurities in Pesticides: A Neglected Source of Contemporary Relevance. *Environ. Sci. Technol.* 44, 5409–5415.

In another study current used pesticides in Australia were screened for unintentionally POPs PCDD/PCDF. PCDD/PCDF were detected in all pesticide formulation with high levels in pentachloronitrobenzene (PCNB) (Holt et al. 2010¹³⁰, Huang et al. 2012¹³¹). PeCBz and HCB were not screened in this study but it was mentioned that PCNB degrades to PeCBz in the environment (approx. 3%) and that this is the largest source of unintentionally PeCBz s higher than all other sources combined (UNEP 2010¹³²).

DRAFT

¹³⁰ Holt E, Weber R, Stevenson G, Gaus C (2010) Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/Fs) Impurities in Pesticides: A Neglected Source of Contemporary Relevance. *Environ. Sci. Technol.* 44: 5409–5415.

¹³¹ Huang J, Yu G, Deng S, Wang B, Wu C, Yamazaki N, Weber R (2012) Determination of PCDD/Fs and DL-PCBs as impurities in Chinese pentachloronitrobenzene pesticides. [Organohalogen Compounds 74, 1429-1432.](#)

¹³² UNEP (2010) Additional consideration of new persistent organic pollutants: pentachlorobenzene. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/21) Geneva 11-15. October 2010.