

October 2004

HORIZONTAL -27
Brominated Flame Retardents

Horizontal Standardisation of Brominated Flame Retardants (BFRs)

Report of the desk study on BFRs with focus on
Polybrominated Diphenyl Ethers (PBDEs)

Ethel Eljarrat, Göran Marsh and Damià Barceló

Department of Environmental Chemistry,
IIQAB, CSIC, Barcelona, Spain



Acknowledgement

This work has been carried out with financial support from the following EU Member States: UK, Germany, France, Italy, Spain, Nordic countries, Netherlands, Denmark, Austria, EU DG XI and JRC, Ispra.

CONTENTS

SUMMARY

1. INTRODUCTION
2. A FRAMEWORK FOR A HORIZONTAL STANDARD FOR PBDEs
 - 2.1 General description
 - 2.2 Pre-treatment
 - 2.3 Extraction
 - 2.4 Clean-up
 - 2.5 Measurement by GC in combination with ECD or MS
 - 2.6 Requirements for identification and calculations
3. EXISTING STANDARDS OR DRAFT STANDARDS
4. EVALUATION OF DRAFTING A HORIZONTAL STANDARD
 - 4.1 Discussion
 - 4.2 Steps to be taken
5. CRITICAL POINT AND RECOMMENDATIONS
6. DRAFT STANDARD (CEN TEMPLATE)

REFERENCES

LIST OF TABLES

LIST OF FIGURES

SUMMARY

This report describes the desk study to the horizontal standardisation of PBDEs. The work is based on a critical evaluation of existing articles and one draft standard.

Important parts in the standard to develop will be decision tables, because it is not possible to make one single working procedure for the matrices involved (waste, sludge and soil).

Especially it will be necessary to have different procedures for extraction and clean-up. To assure reliable and comparable results it will be necessary to set minimum requirements for different steps in the method.

After acceptance of the approach described, a framework can be made that hopefully, can be filled in with procedures already described in existing methods. Limited new procedures will need description. Critical steps in the procedure can be evaluated by pre-normative research before starting a comparison study.

1. INTRODUCTION

The European project HORIZONTAL is focussed on the standardisation of test procedures in environmental samples. The present desk study is a start to elaborate the possibility of horizontal standardisation on polybrominated diphenyl ethers (PBDEs) in sludge, soil and bio-waste.

PBDEs are subject of standardisation in ISO TC147 in sediment and sewage sludge.

Horizontal standardisation should lead to one standard suitable to analyse the matrices waste, sludge and soil.

2. A FRAMEWORK FOR A HORIZONTAL STANDARD FOR PBDEs

2.1 General description

PBDEs are measured in several matrices. For environmental purposes it is necessary that the methods applied in these matrices are comparable and making use of the same principles and instrumentation. Several articles and one draft standard (see Annex 1) are available for the measurements of PBDEs in different environmental matrices. Depending on the properties of the matrix, different or slightly different steps in the method can be necessary. Not all procedures are applicable for all different matrices. In a standard the choices to be made must be clear and hence, a decision structure has to be described. Later on, all the steps that are necessary to analyse in the different matrices can be described in more detail. This should be done by using the technical content in the literature mentioned above. The analysis of PBDEs can be described with the following steps

- Pre-treatment of the sample and preparing of the test portion
- Extraction
- Clean-up
- Measurement by GC in combination with MS
- Requirements for identification and calculations

2.2 Pre-treatment

Pre-treatment is necessary to deliver a homogeneous sample and a sample suitable for extraction. The procedure depends on the material to be treated. Important is the reduction of the water content to less than 25%. There are pre-treatment procedures available for other

organic pollutants than PBDEs such as the PCBs. The horizontal standard for PBDEs should refer to these procedures. Precaution must be paid to PBDEs since they are light sensitive and undergo photochemical degradation, especially the high brominated PBDE congeners.

2.3 Extraction

Bio-waste, sludge and soil may differ in properties and also within one matrix properties may differ very much. For instance, waste can be solid-like, but may also contain plastic residuals. The differences make it impossible to describe one general extraction procedure. Choices in a standard must be clear. The final standard should contain a decision table based on the properties of the sample and the extraction procedure to be described in the standard. Two general extraction lines will be followed, the use of the classical Soxhlet and the more modern ASE (accelerated solvent extraction). Depending on the extraction procedure, an existing pre-treatment procedure should be followed.

2.4 Clean-up

Clean-up is necessary to remove present disturbing components. When they are not present, clean-up is not necessary. If specific disturbing components is present in the samples and need to be removed, different procedures described in the literature may be used.

2.5 Measurement by GC in combination with MS

GC in combination with MS is the most often used combination for measurement of PBDEs. The ionisation techniques negative chemical ionisation (NCI) or electron ionisation (EI) low resolution mass spectrometry (LRMS) can be used. Both ionisation techniques should be included. Internal standards are necessary for quantification in both cases there the use of the isotopic dilution method is applied in EI.

2.6 Requirements for identification and calculations

The principles described in ISO/DIS 22892 (GC-MS identification) will be used for the identification. This standard makes use of identification points as already used in European document.

3. EXISTING STANDARDS OR DRAFT STANDARDS

There is only one standard draft on PBDEs, but there are some general standards that could be applied.

PBDEs:

ISO/TC 147: ISO/CD 22032, Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge by extraction and GC-MS

ISO/TC 190: ISO/DIS 22892, GC-MS Identification

ISO/TC 190: ISO/FDIS 14507, Pre-treatment of soil (organic contaminations)

ISO/TC 190: ISO/CD 22892, Pre-treatment of soil (physico-chemical analysis)

CEN/TC 292 WG5 N0296, Waste: preparation of test portions

ISO/TC 147 ISO/FDIS 5667 part 3 and 15, Water Quality, Sampling

4. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

4.1 Discussion

As described in previous chapters it is not possible to make a standard with single procedures for each separate step that can be used for every sample to be analysed. A horizontal standard has to contain different possibilities. It has to be prevented that everything is allowed.

Multiplying all the different steps will lead to a too large number of possibilities. A solution for this is the introduction of decision tables. Depending on the goal to achieve (extraction, clean-up etc), the table has to give a limited number of different possibilities. This procedure has to be secured with description of effectiveness of procedure. For instance:

- Extraction procedure: The recovery of added PBDE should be at least ..%
- Clean-up shall remove the disturbing components and recovery of PBDE added before clean-up should be at least ..%
- Identification: Use of identification points ask for a minimum effort. This will automatically lead to the right column and detector. If not enough identification points are gained, presence of the PBDE cannot be reported.

Validation of the standard for all matrices on the short term will be difficult (too expensive). This has to be an ongoing process and needs co-ordination, which can be a task for the project HORIZONTAL. Validation may also lead to steps not yet described or excluding a specific

step for a specific matrix. This will make adjusting of the decision tables necessary in new versions of the standard.

4.2 Steps to be taken

As described above it will be necessary to look to the possibilities of pre-normative research to limit the allowed possibilities in the standard. This can be in co-operation with the studies within the Workpackage “Horizontal – Organic micropollutants”.

Pre-normative work will be followed by comparison studies, matrix by matrix. It is expected that a complete validation of the Horizontal standard will be too expensive to do it in one comparison. It will be necessary to set priorities for validation that also will be taken over by European laboratories to assure partition in the comparison study.

5. CRITICAL POINT AND RECOMMENDATIONS

In the approach described in this report, decision tables are a part of the standard. These tables make differences in applied methods possible, depending on the sample. Justification of the method will be assured by setting limits for recovery and prescription of the minimum requirements for identification. This approach has to be discussed within the project HORIZONTAL.

6. DRAFT STANDARD (CEN TEMPLATE)

Will be the result of next step

REFERENCES

See the list of standards in chapter 3

EU, 2002. Commission Decision 12 August 2002. Implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Docnr: C(2002) 3044