Pitfalls in the analysis of brominated flame retardants in environmental, human and food samples – including results of three international interlaboratory studies

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Since the beginning of this century, an increasing number of laboratories have become involved in the analysis of brominated flame retardants (BFRs) in the environment, humans and food. To assure as well as improve the quality of these analyses, a series of international interlaboratory exercises has been organized. It appeared that the differences between the BFRs create more difficulties for their analysis than, for example, that of polychlorinated biphenyls. Problems that arise with the determination of decabromodiphenyl ether and hexabromocyclododecane, due to instability at higher temperatures, high background values and other factors, make their analysis much more demanding than, for example, that of 2,4,2′,4′-tetrabromodiphenyl-ether. A number of these pitfalls can be identified from the evaluation of the interlaboratory study results. We propose analytical solutions for these problems.

Keywords: Brominated flame retardant; Hexabromocyclododecane; Interlaboratory study; Polybrominated diphenyl ether; Tetrabromobisphenol-A

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1. Introduction

There are 75 commercially available brominated flame retardants (BFRs), only a small number of which have been identified in the environment.

The three main representatives are: tetrabromobisphenol-A (TBBP-A), which has the highest production figures world-wide; hexabromocyclododecane (HBCD); and, polybrominated diphenyl ethers (PBDEs). There are three commercial PBDE products: Penta-mix, a blend of tetra-hexa BDEs; Octa-mix, a blend of hepta-nona BDEs; and, Deca-mix, 97% pure deca BDE. Other BFRs that have been identified are: 2,4,6-tribromophenol, a compound that also occurs in nature; and, decabromodiphenylethane, recently identified by Kierkegaard et al. (2004) [1].

Although PBDEs have been found in the aquatic environment since the late 1970s [2–4], little attention was paid to them initially. Only after a report on the presence of PBDEs in sperm whales from deeper Atlantic waters [5] and the apparent increase of tetra-BDE and penta-BDE concentrations in Swedish human milk [6] did laboratories start to develop analytical methods for detecting and quantifying PBDEs in the environment.

PBDEs are very similar in structure to polychlorinated biphenyls (PCBs) [7]. The two congeners that are most frequently reported in biota are BDE 47 (2,4,2′,4′-tetra BDE) and BDE 99 (2,4,5,2′,4′-penta BDE). These congeners most probably originate from the (mainly) historical use of pentabromodiphenyloxide (Penta-mix), commonly used in flexible foam.

Nowadays, decabromodiphenylether (BDE 209) has the largest production volumes of all PBDEs [8]. BDE 209 has been reported to occur in relatively high concentrations in environmental samples, but until now BDE 209 concentrations in aquatic organisms have been low or below detection. Several laboratories have recently started to develop BDE-209 methods.

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An even smaller, but growing, number of laboratories has started to develop analytical methods for HBCD and TBBP-A. A series of world-wide interlaboratory studies was organized to assist these laboratories in their method development. These studies were designed primarily as learning exercises and the laboratories were given advice on the use of the preferred conditions for extraction, clean-up, and gas chromatography (GC). Following the evaluation of each round, advice was also given about further possible analytical improvements.

The results of the first study showed a good agreement between the 20 participating laboratories for the BDEs 47 and 100 (2,4,6,2′,4′-penta BDE), whereas, for other congeners – 99 (2,4,5,2′4′-penta BDE), 153 (2,4,5,2′,4′,5′-hexa BDE), 154 (2,4,5,2′,4′,6′-hexa BDE) and BDE 209, in particular – further improvement was considered necessary [9].

Following this first study, three further studies were organized under QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) for PBDEs, HBCD and TBBP-A. QUASIMEME is a proficiency testing programme, which also organizes learning exercises and training programmes and workshops for ''new'' contaminants. We discuss the trends in the results in this article.

2. Interlaboratory studies

A second international interlaboratory study on the analysis of BFRs in environmental samples was organised between 1 November 2001 and 15 March 2002.

Compared to the first study, the set of target compounds was extended to include BDEs 28 (2,4,4′-triBDE) and 183 (2,3,4,5,2′,4′,6′-hepta BDE), and HBCD, TBBP-A, and dimethyl TBBP-A (MeTBBP-A) because literature reports indicated that these BFRs could be present in environmental samples. BDE 183 is the main representative of the technical Octa-BDE mix.

In addition, a wider selection of environmental test materials, such as lake trout, mussels, sediment, and human milk, was included in the second study.

A clean sediment extract was also included for a more detailed study of sediment analysis.

Two solutions with the target analytes with undisclosed concentrations were also provided to check for possible calibration errors.

The study was a collaborative project of the Bromine Science and Environmental Forum (BSEF), Brussels, Belgium, the Netherlands Institute for Fisheries Research (RIVO), IJmuiden, The Netherlands, and QUASIMEME.

A third interlaboratory study was organised between 1 July 2003 and 1 December 2003. This study was carried out by QUASIMEME, in collaboration with RIVO. The target compounds were identical to those of the second study. This study included the following test materials: sediment; sewage sludge; herring and capelin oils; and, a standard solution containing the target compounds with undisclosed concentrations.

A fourth study, also organised by QUASIMEME and RIVO, was conducted between 1 May and 1 August 2004. The target compounds were identical to those of the second study. Two sediments, two fish matrices (farmed salmon and mackerel), and two standard solutions with the target compounds in undisclosed concentrations were sent to the participants. Table 1 provides an overview of all four studies so far. The statistical evaluation of all studies was based on the new statistical method of Cofino [9,10].

Table 2 summarises the results of the last three studies, showing: the mean values obtained by the statistical model; the number of datasets included (n); the coefficient of variation (CV); and, the λ factor, which shows the percentage of data that is used to calculate the CV. The higher the λ value, the more data are included, so the better the dataset that is described by the CV value. The λ values of the secondary datasets are not shown, as the first λ value normally gives a good indication of the quality of the dataset. For a correct interpretation of the results, it is essential to consider not only the CV value but also the λ value.

It is not easy to identify trends in this type of dataset because there are a number of parameters that vary from round to round. These include the number and the identity of the participating laboratories, the λ values, the concentrations of the determinands in the test material, and the complexity and variations in the analytical methods used by the participants. Because of the relatively large CV values – and/or low associated λ values – obtained for some of the determinands, the variations in concentrations and in the number and identity of the participants – several new participants entered each round – multi-variate statistics fail to identify specific critical parameters. Nevertheless, from the dataset and from experience with interlaboratory studies of other environmental contaminants, a number of specific problems can be identified. We discuss these in the next paragraph. Apart from that, the dataset shown in Table 2 leads to a number of clear observations.

Obviously, the ''Horwitz trend'' is also visible in this dataset – that lower analyte concentrations lead to higher CV values [11]. Some random, vivid examples (Table 2) were:

- Round 2, BDE-153 concentration in lake trout – 2.2 ng/g – and the associated CV – 31%; and, BDE-153 concentration in mussels – 0.06 ng/g – and the CV – 55%;
- Round 2, human milk results – all BFRs showed low concentrations and high CV values;
- Round 3, BDE-154 concentration in herring – 0.31 ng/g – and the CV – 13%; and, BDE-154 concentration in capelin oil – 0.03 ng/g – and the CV – 59%;