

INTERLABORATORY STUDY ON DECA-BDE ANALYSIS IN ENVIRONMENTAL SAMPLES INVOLVING ROUTINE LABORATORIES

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Introduction

In September 2005, the EU-project NORMAN has been launched in order to establish a network of reference laboratories and related organisations dealing with the monitoring of emerging environmental pollutants (<http://www.norman-network.de>). The network provides a platform for the exchange of information and data on emerging pollutants between monitoring laboratories, research centres, competent authorities, and end-users across the European Union. The main objective of this network is to support risk assessment by ensuring the quality and comparability of data. For that purpose, validation protocols have been developed specifically designed to support the harmonised optimisation and validation of analytical methods for monitoring of emerging pollutants.

In order to test the developed validation protocols and the ability of the network to meet European demands for monitoring of emerging pollutants, three interlaboratory studies have been undertaken.

One of the three case studies, which have been conducted within the EU-project NORMAN had the aim to test the protocol for method validation at the routine level and to transfer knowledge from expert to routine laboratories. Decabromodiphenyl ether (decaBDE), an emerging pollutant that belongs to the group of brominated flame retardants, seemed to be a proper model compound for this case study. On the one hand there is the need for monitoring according to the recently completed risk assessment¹ and on the other hand the laboratory performance in decaBDE analysis needs still to be improved^{2,3}.

A first interlaboratory study with expert laboratories was performed in order to identify the crucial steps in the analysis of decaBDE⁴. On the basis of the results of this exercise a detailed method description was elaborated to enable monitoring laboratories not specialised in the analysis of brominated flame retardants to determine decaBDE in environmental samples with reasonable accuracy. Then, early in 2008 a second intercomparison study was conducted involving laboratories with different levels of expertise to test the developed harmonised protocol at routine level. Here we report the results of this intercomparison and discuss them in respect of the possibility to transfer of knowledge from research to routine laboratories.

Materials and methods

Compared to the 2006 interlaboratory study⁴, the set of test materials was extended by a low contaminated sediment sample to cover different concentrations and sample types. The sediment sample was taken from the river Elbe (Preloc, Czech Republic) in 2005, wet sieved (<63µm), freeze dried, and homogenized. Moreover, a high contaminated dust sample and a standard solution of undisclosed concentration were distributed. The sediment sample and the standard solution were provided by the Institute for Environmental Studies at VU University. The house dust sample was the reference material NIST 2585 recently certified for its PBDE content⁵. This reference material is a sterilized, freeze-dried and sieved (< 100 µm) house dust collected from vacuum cleaner bags from homes, motels, and hotels. It contains polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlorinated pesticides, and polybrominated diphenyl ethers.

Prior to the interlaboratory study, a meeting with the participants was held addressing difficulties in decaBDE analysis, experiences from the first round, and recommendations from the literature^{6,8}. The laboratories were advised on the preferred conditions for extraction, clean-up, and gas chromatography.

Each laboratory used its own analytical methodology. For the final determination, GC/MS operated in either electron ionisation (GC/EI-MS) or electron-capture negative ionization (GC/ECNI-MS) mode was applied. Any

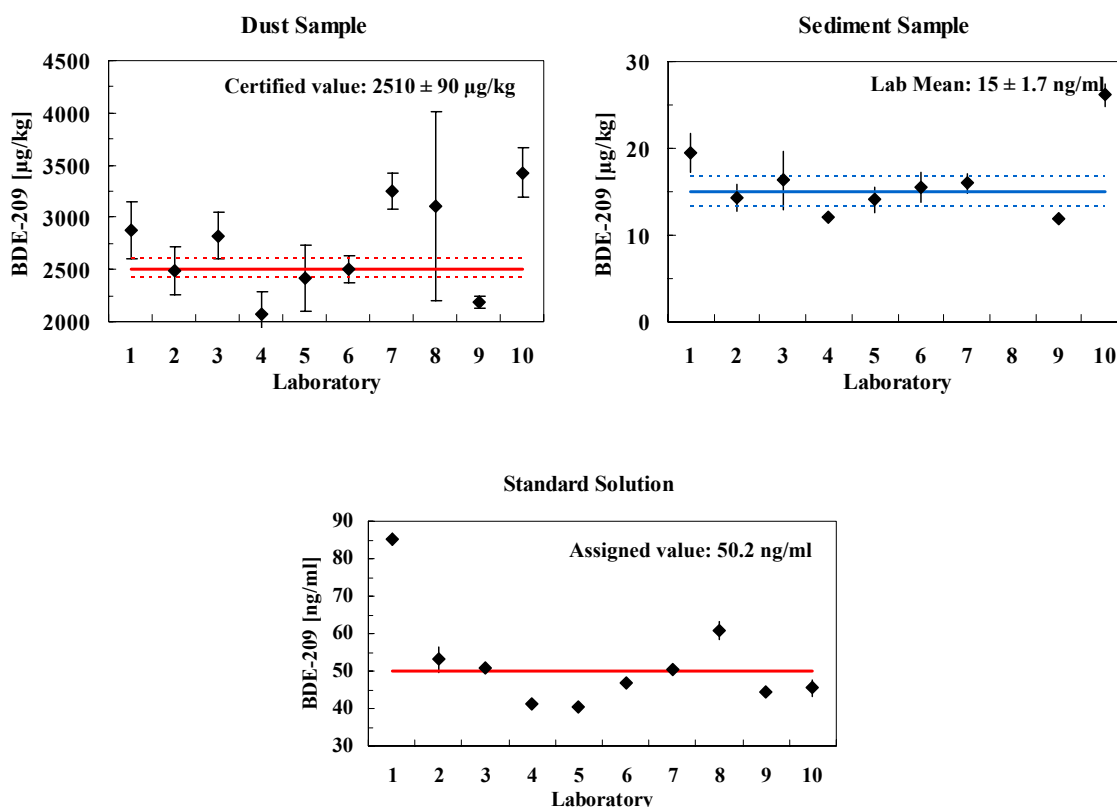
appropriate extraction and clean-up method was allowed to be used. Four replicate analyses of each sample were requested. Because of known blank problems in decaBDE analysis, participants were asked to determine four independent blank replicates. All participants agreed upon the use of $^{13}\text{C}_{12}$ -labelled decaBDE as internal standard. This was regarded a fundamental condition for reliable analytical results. Participants were also requested to keep records on each single step of the whole analytical procedure and any circumstances that might have influenced the results.

Statistical evaluation of results was carried out using ProLab (quo data Ltd., Dresden, Germany) based on the requirements of the German Standard DIN 38402-42 and ISO 5725-2, respectively.

Results and Discussion

As reflected in the first interlaboratory study⁴ a variety of possible options to analyse PBDEs are applicable. Thus, each of the ten participating laboratories applied a different analytical method. All participants used separation conditions specifically optimised for the analysis of decaBDE in accordance with the provided instructions. The internal standard $^{13}\text{C}_{12}$ -BDE-209 was added prior extraction by all participants. Different extraction techniques like pressurised liquid extraction, soxhlet or ultrasonic extraction were applied using different solvents and mixtures of solvents. The obtained extracts were purified applying various clean-up techniques. The laboratories used non-polar GC columns of 15 m length or less with an internal diameter of 0.25 mm, and a film thickness of 0.1 or 0.25 μm . PTV/splitless with or without pressure pulse or splitless injection at moderate injector and column temperatures $< 300\text{ }^\circ\text{C}$ were predominantly applied.

Figure 1: Means of four replicates and standard deviations of decaBDE concentrations in dust (NIST 2585), sediment sample and standard solution reported by ten laboratories (no elimination of outliers)



Results summarized in Figure 1 indicated, that the participants did not had any appreciable difficulties with the analysis of decaBDE in the intercomparison samples. The average recovery obtained by the participating laboratories was 109 % for the dust sample and 96 % for the standard solution. One laboratory did not report results for the sediment sample, as sulphur presumably interfered with the analysis. Prior to statistical evaluation, outliers were removed according to ISO 5725. One individual within-laboratory outlier (one out of four results deviated significantly) was removed from the results for the dust sample. One between-laboratory outlier (significant deviation of the laboratory mean from the total mean) was eliminated from the results for the standard solution and the sediment sample, respectively.

Table 1: Performance Characteristics for the Second Interlaboratory Study “Determination of DecaBDE in Environmental Samples” conducted within the EU-Project NORMAN

Sample	l	n	n_{AP} %	x	s_R	CV_R %	s_r	CV_r %
Dust	10	40	2.5	2740	535	19.5	212	7.7
Sediment	9	36	11.1	15	2.9	19.4	1.8	11.9
Standard Solution	10	40	10	48	6.5	13.6	1.7	3.6

- l Number of laboratories
 n Number of single results
 n_{AP} Percentage of outliers
 x Total mean after elimination of outliers [$\mu\text{g}/\text{kg}$ or $\mu\text{g}/\text{ml}$]
 s_R Reproducibility standard deviation [$\mu\text{g}/\text{kg}$ or $\mu\text{g}/\text{ml}$]
 CV_R Reproducibility variation coefficient [%]
 s_r Repeatability standard deviation [$\mu\text{g}/\text{kg}$ or $\mu\text{g}/\text{ml}$]
 CV_r Repeatability variation coefficient [%]

As presented in Table 1, the reproducibility variation coefficients were 20 % (dust sample), 19 % (sediment sample) and 14 % (solution sample). The repeatability variation coefficients were less than 12 % for all samples. Compared to the first round, in which relative reproducibility standard deviations of less than 10 % were achieved for dust as well as the standard solution, results were somewhat worse. However, taking into account that the level of expertise of the laboratories was variable and some laboratories had just recently established methods for decaBDE analysis, the results look very promising. This denotes that the performance of the participating laboratories in decaBDE analysis was surprisingly good compared to that seen in previous international interlaboratory studies. Those studies revealed that satisfactory results were difficult to achieve especially for inexperienced laboratories^{2,10}. Also in the recent International Laboratory Performance Study on the Analysis of Brominated Flame Retardants in Environmental Samples organised by QUASIMEME, a relatively high and unsatisfactory CV of 74 % was obtained for marine sediment containing approximately 6 ng/g of decaBDE⁹.

The results of the interlaboratory study conducted within the NORMAN project indicated that all laboratories followed the recommendations on how to recognise and eliminate possible sources of errors. For the determination of decaBDE, several methods for extraction and clean-up are appropriate, which is consistent with the findings from the first round. Obviously, the choice of the analytical method is less important than the careful control of critical factors like thermal and photochemical degradation of decaBDE as well as blanks. The method performance study showed that routine laboratories are able to analyse decaBDE in environmental samples with acceptable accuracy provided they have adjusted their methods according to the current best practice with special emphasis on QA/QC issues. The NORMAN project taught us that laboratory performance in the analysis of emerging contaminants at the routine level can be improved distinctly by transfer of knowledge from expert to

routine laboratories by means of workshops, the provision of harmonised analytical protocols and proper training.

Acknowledgements

This work was funded under the 6th Framework Programme — Priority 6.3 "Global Change and Ecosystems" (Contract N° 018486 – project NORMAN, Start date 1st September 2005). The authors acknowledge financial support by the European Commission under the project MODELKEY (511237-GOCE) that supplied the sediment sample. We thank all participating laboratories of the interlaboratory study for the excellent cooperation.

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