Round 2 Interlaboratory Study - CASE Study 3 on DecaBDE in Sediment and Dust

Instruction Protocol

Materials

The **sediment** sample is a sieved (<63 µm), freeze dried and homogenised river sediment (Elbe, Germany). It contains polycyclic hydrocarbons, polychlorinated biphenyl congeners, chlorinated pesticides, and polybrominated diphenyl ether congeners. The bottle contains approximately 30 g of material. The sediment is low contaminated with BDE209 in the µg/kg range.

The **dust** sample is a sterilized, freeze dried and sieved (< 100 µm) house dust from vacuum cleaner bags collected from homes, motels, and hotels. It contains polycyclic hydrocarbons, polychlorinated biphenyl congeners, chlorinated pesticides, and polybrominated diphenyl ether congeners. The bottle contains approximately 4 g of material. The dust is high contaminated with BDE209 in the mg/kg range.

A **GC - test solution** of BDE-209, dissolved in toluene in undeclared concentration is provided to check for calibration errors. Its concentration is in the range of 25 to 100 ng/ml.

Homogeneity, stability and storage

The materials have been shown to be homogeneous and stable for the purpose of the test. The sediment and dust materials must be stored at temperatures between 15 °C to 30 °C away from direct sunlight. The GC-test solution should be stored at 4 °C protected from light.

Analysis

The materials are of naturally occurring river sediment and house dust and may contain constituents of unknown toxicities; therefore, caution and care should be exercised during its handling and use.

Prior to removal of subsamples for analysis, the contents of the bottle should be homogenised. The sediment and dust sample should be dried to a constant mass before weighing for analysis, to determine the concentration on a dry mass basis. Another possibility is the determination of the moisture content.

The samples should be analysed using routinely applied validated methods and procedures. Any appropriate extraction and cleanup method may be used. The use of **^{13}C-BDE-209** as an internal standard is **obligatory**. All measurements should be performed by using GC/MS operated in either electron impact (GC/EI-MS) or electron capture negative ionization (GC/ECNI-MS) mode. Some advice on how recognise and avoid possible sources of error is given in the Standard protocol (see enclosed). A short GC column of 15 m or less is **obligatory** to use for the analysis.

Replicates

Please determine **four** independent replicates with the **sediment** using a sample intake of 5 to 7 g of the sediment material.

Please determine **four** independent replicates with the **dust** using a sample intake of 0.1 to 0.5 g of the dust material.

The **GC - Test solution** should be analysed after having added an appropriate amount of the Internal Standard (^{13}C-BDE-209) which matches the expected concentration range (25 - 100 ng/ml). The prepared solution should be injected **four** times.

Because of the blank problem please determine **four** independent **blank** replicates. The treatment of the blanks should be identical to that of the sediment and dust sample (e.g. residence time at the bench).

Reporting of results

For the sediment and dust sample the results should be expressed on a dry weight basis (µg/kg). Results for the GC test solution should be given in ng/ml.

Please enter your analytical data and method characteristics using the provided files (provided by email). You should report all of the requested methods details by filling in the questionnaire.

The **results** of the sediment and dust and the GC – Test solution are to report by using Excel-file "Results of dust, sediment and GC test solution.xls" and Word-document "Experimental conditions.doc". Please send the completed files to Pim Leonards by email (pim.leonards@ivm.vu.nl) until **15 March 2008.**

Please also send a typical **GC–chromatogram** of the sediment, dust sample and the GC-test solution with the drawn integration marks (either by email or in a printed version). Report results of blanks separately and do not include blanks in calculations!

Standard Protocol

Determination of BDE-209 in sediment and house dust

Principle

A proper test portion of the dried sediment or dust sample is extracted with an organic solvent by an appropriate extraction technique (e.g. soxhlet extraction, PLE, sonication, shaking). The obtained extract is concentrated and cleaned-up. Sample cleanup procedures may include sulphuric acid treatment, GPC, column chromatography on alumina, florisil or silica. For the sediment sample sulphur should be removed (e.g. active copper powder or TBA reagens). The purified extract is analyzed by high resolution capillary gas chromatography combined with mass spectrometry operated in the electron ionisation or electron capture negative ionisation mode. Quantification is conducted by the internal standard method using $^{13}C_{12}$ labelled Decabromodiphenyl ether as internal standard.

The International Standard ISO/DIS 22032 “Water quality - Determination of selected polybrominated diphenylethers in sediment and sewage sludge - Method using extraction and gas chromatography/mass spectrometry” is recommend as a guidance for the analysis of the test material. Special attention should be paid on following issues:

Problems	**Solutions**
Photodegradation under influence of direct sunlight	Use of UV filters at laboratory windows and at fluorescent lightings Use of amber glassware (or covered with e.g. aluminium foil)
Poor solubility	Check solubility in the organic solvent before preparing stock solutions or preparing highly concentrated extracts. BDE209 dissolves well in toluene. It should be avoided that the extracts would be evaporated until dryness, because decaBDE may not completely re-dissolve after that step. During concentration, use toluene as a keeper.
Blank problem (decaBDE may be present in dust in the laboratory or as contamination of the glassware)	The laboratory should be kept as clean as possible. Introduction of most types of packing materials in the lab should be avoided. All open glassware should be covered, e.g. by aluminium foil, to prevent dust particles to enter solutions or samples. Cleaning of glassware by heating at 420 °C and rinsing with toluene prior use Blank analysis should be carried out more frequently than usually. The treatment of the blanks should be identical to that of the sample (e.g. residence time at the bench). The use of a ^{13}C internal standard is highly recommended, and the sensitivity of the detector should be fully optimized.
Thermal degradation	Short (< 15 m) and narrow (< 0.25 mm) GC columns with thin films (0.1 µm), moderate injector (e.g. 275 °C) and column temperatures (< 300 °C), and short injector residence times, or cold injectors. Splitless injection is critical and can only be applied successfully when combined with pressure pulse or by using short splitless time. On column injection may a suitable alternative.