Quality in POP Analysis

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The session comprises 18 papers on quality assurance and quality control (QA/QC) regarding the determination of dioxins and other halogenated POPs in a wide range of sample types. Method validation, use of certified reference materials and interlaboratory studies are the main subjects of the papers submitted to this session.

A thorough method validation is required when changing or using different analytical methods and procedures for the determination of POPs. Validation of analytical methods is discussed in 3 papers describing the determination of POPs in different sample types.

An analytical method for PBDEs in breast milk using GC-HRMS showed good results for all BDEs including DecaBDE (Päpke et al.). For the most abundant BDEs #47, #99 and #153 the RSDs were below 10%, for DecaBDE the RSD was 22%. A GC-LRMS method using ^{13}C internal standards for the determination of both hexachlorobutadiene and chlorobenzenes in tri- and tetrachloroethene showed good sensitivity, recovery and repeatability (Chiu et al.). The determination of dioxins in environmental samples including the estimation of uncertainties in the working range of 0.2-1000 ng/kg is presented by Carvalhaes et al. In addition 4 papers discuss the implementation of different analytical techniques including the use of accelerated solvent extraction (ASE) for dioxins in foods of vegetable origin (Hori et al.), the use of ASE and GC-ECD for screening PCBs in food of animal origin (Piersanti et al.), the use of solid-phase extraction for the analysis of dioxins in human serum (Pérez et al.) and a comparison of five different extraction methods for the determination of PCBs in sediment (Numata et al.).

Further improvement of analytical techniques for the determination was POPs is described in another 3 papers. The analysis of chlorinated paraffins (CPs) is described by Reth et al. They obtained significant improvements of the results by NCI-MS/MS using the linear dependence of the total response factors on the chlorine content. New indicator PCBs are proposed by Ishikawa et al. after carefully studying PCB profiles from commercial PCB mixtures, indoor air samples and emission gasses from both a MSWI and cement plant. An improvement of the commonly used spiking protocol of method 1613 is presented by Martin et al. Instead of adding the ^{13}C spikes dissolved in acetone directly into water samples, they used equilibration of water samples with spiked sand.

A good quality assurance plan is invaluable for securing the quality and traceability of environmental analytical data within a project and thereby improving the outcome of a project. Byrne et al. describe in detail the outline of QA Project Plans required for projects implemented under the USEPA Dioxin Exposure Initiative.

Certified reference materials are important QA/QC tools for assessing the trueness of analytical results. Standard reference materials (SRMs) of POPs in biological tissue, marine sediment and particle-related material, available from NIST, are described by Poster et al. Newly developed SRMs for PCBs and organochlorine pesticides in mussel tissue are presented in detail.

Interlaboratory comparison exercises on the determination of POPs in various matrices have been performed on a national and international basis for some time. Such studies are an important QA/QC instrument for laboratories and stimulate to improve the analytical performance. They further demonstrate the readiness of laboratories to perform good analyses. In the session, results are presented from five different interlaboratory comparison studies.

Van Bavel et al. presents an interlaboratory study on chlorinated/brominated PXDDs/Fs in fly ash with 25 participants world-wide of which 12 were able to report data before the deadline. Results from the 3rd round of the interlaboratory study on brominated flame retardants in biota, sediment and sludge within the QUASIMEME programme are described in a paper by de Boer and Wells. Special care was taken to improve the results for DecaBDE, TBBP-A and HBCD. Results from a study on both PXDDs/Fs and PBDEs in sediment and fly ash in Japan are discussed in a paper by Takahashi et al. In total 10 laboratories participated in this study and 5-8 were able to report results for the different compounds and samples including air dried sediment and animal fat. Results from a large interlaboratory study on PCDDs/Fs and dl-PCBs in sediment and fly ash in Japan showed excellent results after omitting outliers with a z-score higher than 2 (Shiozuki et al.) for a fly ash extract distributed to 83 participants (RSD on TEQ basis 4.4%). Five rounds of Japanese interlaboratory studies on PCDDs/Fs and dl-PCBs in food are summarized by Matsuda et al. There was good agreement between the 6 to 15 participating laboratories with RSDs on TEQ basis ranging from 6.6 to 31% depending on the type of sample and concentration.

A new method for the determination of target standard deviations used for the calculation of z-scores in interlaboratory studies on dioxins in food is discussed by Eppe et al. Especially when measuring close to the detection limit a pre-established RSD value (e.g., 20%) might be a too strict criterion. Using a recently developed function describing the relation between the RSD and the levels of PCDD/DFs present in the samples, RSD values are proposed from 11.9% for levels of 100 ppt to 45.7% for levels of 0.05 ppt.