

## **Abstract**

An analytical method comprised of automated solid phase extraction and determination using gas chromatography electron capture mass spectrometry has been developed for the determination of 12 polybrominated diphenyl ethers (PBDEs), 26 polychlorinated biphenyls (PCBs), two organochlorine compounds (OCs) and two brominated phenols in human serum. The analytes are extracted using a sorbent of polystyrene-divinylbenzene and an additional clean-up is performed on a sulphuric acid silica column to remove lipids.

The method has been validated by spiking horse serum at five levels in the range of 1.2-120 pg PBDEs/g serum, (12-1200 pg BDE-209/g serum), 1.2-120 pg pentabromophenol (PeBP)/g serum, 2.4-240 pg tetrabromobisphenol-A (TBBP-A)/g serum and 3-300 pg PCBs/g serum. Different internal standards were evaluated for the PBDEs. The accuracy given as recovery relative to internal standards, was from 64-150% with relative standard deviations (RSD) ranging from 0.6-56% for the PBDEs. The mean accuracy was 95% and the mean RSD 6.9%. The accuracy for the PCBs was in the range of 29-127% with RSD in the range of 0.3-77%, and with mean accuracy and RSD of 99% and 8.7% respectively. The two OCs hexachlorobenzene and octachlorostyrene had accuracies in the range of 62-104% with RSD in the range of 3.2-15%, the mean accuracy was 93% and the mean RSD 7.5%. The accuracy for the determination of PeBP and TBBP-A were in the range of 77-132% with RSD from 4.5-24%, the mean accuracy and RSD was 109% and 15% respectively. In summary, the overall accuracy and RSD was about 98% and 8.4% respectively. Estimated limits of detection (LOD, signal to noise ratio =3) were in the range of 0.2-1.8 pg/g serum for the PBDEs and phenols, the PCBs and OCs had LODs in the range of 0.1-56 pg/g serum. The method linearity was determined by plotting the concentration of persistent organic pollutants found in the spiked validation samples against the concentration added. Correlation coefficients were in the range of 0.9981-1.0000.

The validated method has been used to investigate the levels of PBDEs and PCBs in pooled serum samples from men (age 40-50 years) sampled in the time period 1977 to 2003, and in pooled serum samples from different age groups sampled in 2002 (all from the general Norwegian population). The sum of seven PBDE congeners (IUPAC No. 28, 47, 99, 100, 153, 154 and 183) has increased from 1977 (0.61 ng/g lipids) to 1998 (4.85 ng/g lipids). From 1999 to 2003 the concentration of PBDEs seems to have stabilized. However, the congener BDE-153 was found to increase throughout the entire period. On the other hand the sum of five

PCBs (IUPAC No. 101, 118, 138, 153 and 180) have decreased steadily from 1977 (665 ng/g lipids) to 2003 (176 ng/g lipids). A comparison was made between the main congeners from PCBs and PBDEs, and it was found that the level of CB-153 was about 46 times higher than the level of BDE-47 in the serum pool from 2003.

In samples from 2002 an increase with age was observed for the PCBs. The highest levels were observed in the age group >60 years where the sum of five PCBs were 308 ng/g lipids and 353 ng/g lipids for women and men, respectively. For the PBDEs the exact opposite trend was observed, with the highest levels in the lowest age group (0-4 years), where the sum of seven PBDEs was 10.4 ng/g lipids. TBBP-A and BDE-209 were detected in almost all samples, but no similar trends to that seen for the PBDEs and PCBs were observed for these compounds.