

## Analytical Method for PBDD/Fs, PBDE and Applications to Environmental Sample

Jae-Won Choi<sup>1</sup>, Shunji Hashimoto<sup>1</sup>, Noriyuki Suzuki<sup>1</sup>, Jun Onodera<sup>2</sup>, Hiroyasu Ito<sup>1</sup> and Masatoshi Morita<sup>1</sup>

<sup>1</sup> National Institute for Environmental Studies, Onogawa 16-2, Tsukuba, Ibaraki 305-8506

<sup>2</sup> Application & Research Center, JEOL Ltd., Musashino 1-2, Akishima, Tokyo 196-8558

Polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) are planar tricyclic aromatic compounds such as chlorinated dioxins (PCDD/Fs). As 2378-TCDD-like effects, 2378-TBDD causes wasting syndrome, thymus atrophy, and liver toxicity and some information was also available on other PXDD/Fs. These compounds are often formed in the process of manufacturing brominated flame retardants (BFRs) such as PBDEs, TBBPA, and waste incinerators for BFR contained materials. There have been very few experimental data on the physical and chemical properties of PBDD/Fs compared to reports on PCDD/Fs. Because of a lack of reference standards, complete identification of each PBDD/F congener is still limited. In the present study, we improved the analytical method for from tetra- to hexa-brominated congeners and applied to environmental samples.

Using <sup>13</sup>C<sub>12</sub>-labelled and unlabelled PBDD/Fs and PBDEs, which are known as disturbances in the identification of PBDF congeners, column chromatography for elution profile was investigated on; (1) multilayered-silica gel column, (2) florisil column and (3) active carbon impregnated with silica gel and copper column was added in the applications to environmental samples. Dried marine sediments were extracted in a Soxhlet apparatus for measurement of PBDD/Fs and PBDEs. To calibrate a micro-syringe, <sup>13</sup>C<sub>12</sub>-OCDD was added prior to HRGC/HRMS quantifications. Analyses of PBDEs and PBDD/Fs were performed on an HRGC-HRMS (HP6890- JMS 700K, JEOL co., Japan) with selected ion monitoring (SIM) mode. HRMS was operated in electron impact mode at a resolution R>12,000 (10% valley).

In the elution test, the recoveries of PBDD/F and PBDE were >90% for multilayered-silica gel column and florisil column. PBDE was separated completely from PBDD/F on a florisil column. However, small amounts of selective PBDE congeners such as BDE47 were found in the PBDD/F fraction in applications to sediments. Further separation was carried on carbon column and elution of PBDE was terminated at 150mL of 25% CH<sub>2</sub>CL<sub>2</sub> / hexane (v/v). Remained PBDD/F was eluted in toluene fraction. Concentrations of PBDE ranged from 60 - 1300 pg/g dry wt in the sediments. Some 2378-substituted PBDD/F congeners also found in the samples and the concentration of PBDD/F was much lower than that of PBDEs. There were still unidentified peaks found in the mass channel of PBDD and PBDF. For further identification of each PBDD/F congeners in environmental samples, more information is needed especially for non-2378 substituted congeners.