Elimination of Chlorinated Methoxybiphenyls as Contaminants in Environmental Samples and as Potential Interferences in the Determination of Chlorinated Dibenzo-*p*-dioxins

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Dioxins (polychlorinated dibenzo-*p*-dioxins, PCDDs) are extremely toxic and mutagenic substances. However, it has been difficult to measure PCDDs in the field of environmental and biochemical studies because of their extremely low contents in samples, poor availability of standard materials, and their many isomers.

Recently, Phillipson and co-worker have pointed out the interferences of polychlorinated methoxybiphenyls (PCMBs) in the determination of PCDDs in PCB-contaminated carp by GC-MS. As PCDDs and PCMBs give the same molecular ion $184 \cdot (m+n) + Cl_{m+n}$, it is impossible to distinguish between PCDDs and PCMBs by monitoring the ions. In addition, it is difficult to separate PCDDs from PCMBs by chromatographic methods.

In this study, two reagents (BF_3 and HI) were examined for the conversion of PCMBs into polychlorinated hydroxybiphenyls, which are easily removed by column chromatography. The use of BF_3 gave good results, with a low reaction temperature (room temperature) and a short reaction time.

In this experiment, 11 PCMBs (Cl_3 - Cl_5) and 6 PCDDs (Cl_2 - Cl_4 , Cl_7 , Cl_8) containing 2, 3, 7, 8-TCDD were examined. The procedure for decomposition of PCMBs was as follows. One ml of 10% BF_3 CH_2Cl_2 solution was added to the residue from the sample extract and the mixture was allowed to stand at room temperature for 30 min. Water was added gently to destroy excess BF_3 , then the sample was extracted three times with 5 ml of hexane. In this treatment, PCMBs were decomposed completely and PCDDs were recovered quantitatively.

A typical method for determination of 2, 3, 7, 8-TCDD in fish and sediment is as follows. Ethanol and KOH were added to the sample and refluxed for one h. The mixture was cooled to room temperature and water was added. The sample was then extracted three times with hexane. The hexane solution was treated three times with conc. H_2SO_4 , rinsed with water, dried and concentrated. The residue was subjected to florisil column chromatography (hexane, 4% ether/hexane). The effluent was concentrated and evaporated to dryness under N_2 stream. Then 10% BF_3 CH_2Cl_2 solution was added to the residue and the mixture was treated as described above. The hexane solution obtained was dried, and evaporated to dryness. The residue was redissolved in hexane and subjected to aluminum column chromatography (hexane, 3% CH_2Cl_2 /hexane, 10% CH_2Cl_2 /hexane). The effluent was concentrated to 1 ml for GC-MS analysis. For mass fragmentography (m/z : 320, 322, 324), a 3% Silicone OV-17, glass column, 3 mm $\times$ 1 m, was used.