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Identification of the Flame Retardant Tetrabromobisphenol-A in the River Sediment and the Mussel Collected in Osaka

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Bromine-containing aromatic compounds are widely used as flame retardants for synthetic polymers and plastic products. There are several reports on the environmental pollution by these compounds. It was reported that polybrominated biphenyls (Fire Master BP-6) had accidentally entered to food supply and caused a serious environmental contamination at Michigan in the USA in 1973 (CARTER 1976 and DICARLO et al. 1978). The residues of pentabromotoluene in sewage sludge were reported in Sweden by Mattson et al. (1975). Polybrominated biphenyl ethers were also found in the tissue of fish from a water system in southern Sweden (ANDERSON & BLOMKVIST 1981).

This paper describes the identification of tetrabromobisphenol-A (TBBP, Fig. 1-(A)) in the river sediment and of dimethyl ether derivative of TBBP (TBBP-DM, Fig. 1-(B)) in the mussel collected at Osaka in Japan. TBBP is known as a most suitable flame retardant for epoxy and polyester resins. In Japan the consumption of TBBP was about 1,500 tons in 1976, which was the largest amount used when compared with those of the other brominated flame retardants.

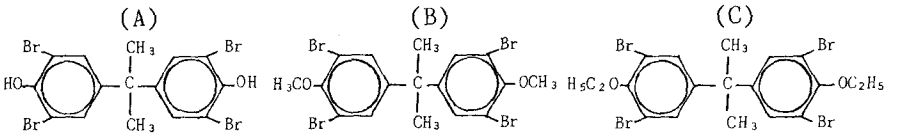

Figure 1. (A). Structure of TBBP. (B). Structure of TBBP-DM. (C). Structure of TBBP-DE.

EXPERIMENTAL

Materials. A river sediment was collected at the downstream of the Neya River, a tributary of the Yodo River which empties into Osaka Bay, in September 1981. Mussels (*Mytilus*

edulis) were collected at the seashore in Osaka Bay in October 1981.

Chemicals. All chemicals used were of analytical grade. TBBP was recieved as a gift from Daihachi Chemical Co. (Osaka, Japan). A reference standard for TBBP-DM was prepared from TBBP by methylation with dimethyl sulfate in basic media.

Analytical method for TBBP. TBBP was converted to diethyl ether derivative (TBBP-DE, Fig. 1-(C)) by ethylation. TBBP-DE was identified and determined by gas chromatographic (GC) and gas chromatography/mass spectrometric (GC/MS) analysis.

Fifty g of wet sediment was mixed with distilled water (25 ml) and copper powder (10 g). The mixed sample was homoginized and extracted with acetone (50 ml x3). The combined extract was added with 500 ml of 2% sodium chloride solution and adjusted to pH 10 - 11 with 1N potassium carbonate. The basic solution was washed with hexane (100 ml x3) in order to remove non-polar substances, i.e., polychlorinated biphenyls and organochlorine pesticides. After adjusting to pH 2 - 3 with 1N hydrochloric acid, the aqueous solution was extracted with a mixture of hexane and diethyl ether (2:1, 100 ml x3). The combined extract was dried with anhydrous sodium sulfate and concentrated to about 0.5 ml. Ethylation of the extract was carried out using ethyl bromide according to the method reported by MIYAZAKI et al. (1981). The resultant mixture was then added with 50 ml of 2% sodium chloride solution and extracted with hexane (25 ml x3). The combined extract was concentrated and treated with concentrated sulfuric acid prior to GC analysis. Further purification was carried out on a florisil column (glass column: 7 mm x 25 cm. florisil: 2 g activated at 130°C over night). The column was washed with 50 ml of hexane and then eluted with 50 ml of a hexane/diethyl ether mixture (v/v, 9:1). The eluate was concentrated to a suitable volume for GC/MS analysis.

The method described above was also used for the extraction and clean-up of TBBP in the shucked mussel, using 20 g of tissue.

GC analysis was carried out using a Varian 2100 gas chromatograph equipped with an ECD (^{63}Ni) and a 2 mm x 1.8 m glass column packed with 2% OV-1 on 100 - 120 mesh Gas Chrom Q; column temp: 235°C, N_2: 35 ml/min. GC/MS analysis was performed on a JEOL JMS DX-300 mass spectrometer connected to a Hewlett Packard 5710 A gas chromatograph and a JEOL JMS 3100 data system. A column (2 mm x 1.8 m) of 2% OV-1 was used. Electron impact ionization voltage was 70 eV with an ion source temperature of 250°C.

Analytical method for TBBP-DM in the mussel. The procedures for the extraction and the clean-up of TBBP-DM in the mussel was refered to the method previously described for the analysis of polybrominated anisoles in fish and shellfish (WATANABE et al. 1983). Briefly, TBBP-DM was extracted with a mixture of hexane and acetone from the mussel samples. Fat was removed by the florisil dry-column method. Then, a florisil wet-column clean-up was carried out. TBBP-DM was eluted with hexane/diethyl ether mixture together with several chlorinated pesticides from the column. The eluate was treated with concentrated sulfuric acid and subjected to GC and GC/MS analysis. The measurment conditions of GC and GC/MS for TBBP-DM were the same as those of TBBP.

RESULTS AND DISCUSSION

TBBP in the river sediment and the mussel. Fig. 2 shows the gas chromatograms of the extract of river sediment and TBBP standard after ethylation. The corresponding peak (peak a) to authentic standard was found in the gas chromatogram of mussel sample (Fig. 2-(B)). Peak a was identified as TBBP-DE by comparing the mass spectrum of peak a with that of TBBP-DE standard (Fig. 3). The residue level of TBBP in this sediment was about 20 µg/kg (ppb) on dry weight basis by GC determination.

On the other hand, TBBP was not detected in the mussel.

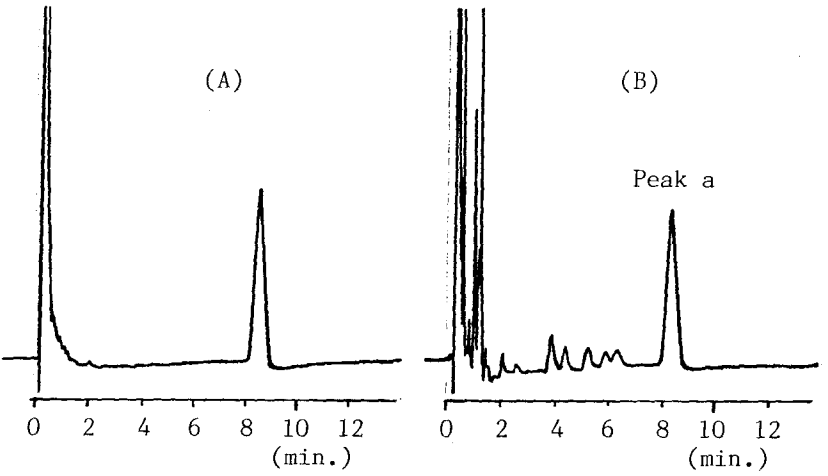

Figure 2. (A). Gas chromatogram of TBBP standard after ethylation. (B). Gas chromatogram of the extract of river sediment after ethylation.

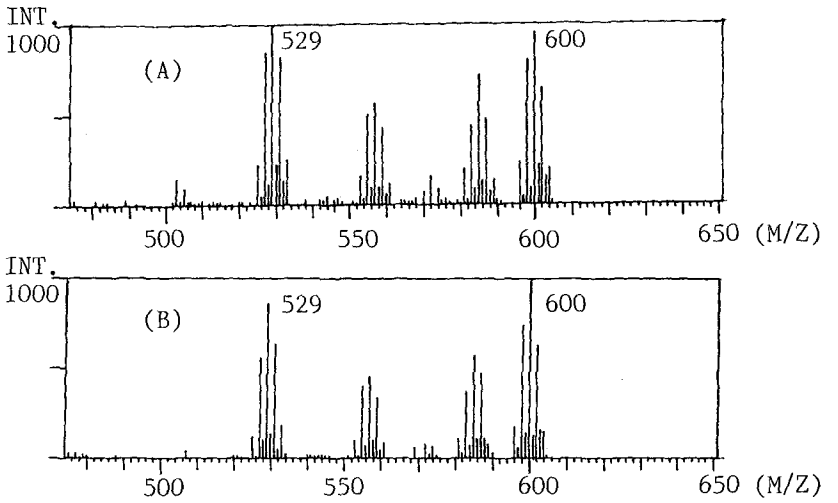

Figure 3. (A). Mass spectrum of TBBP-DE standard.
(B). Mass spectrum of peak a in Fig. 2-(B).

TBBP-DM in the mussel. As shown in Figures 4 and 5, TBBP-DM was identified in the mussel by GC and GC/MS analysis. The residue level of TBBP-DM in the mussel was about 5 ppb on wet weight basis. This TBBP-DM might had been formed from TBBP by chemical or biological reactions in the environment and subsequently was accumulated in the mussel. ROTT et al. (1979) had reported that pentachloroanisole was formed from pentachlorophenol by microbial transformation. Therefore, it is probable that TBBP-DM is also formed by microbial trans-

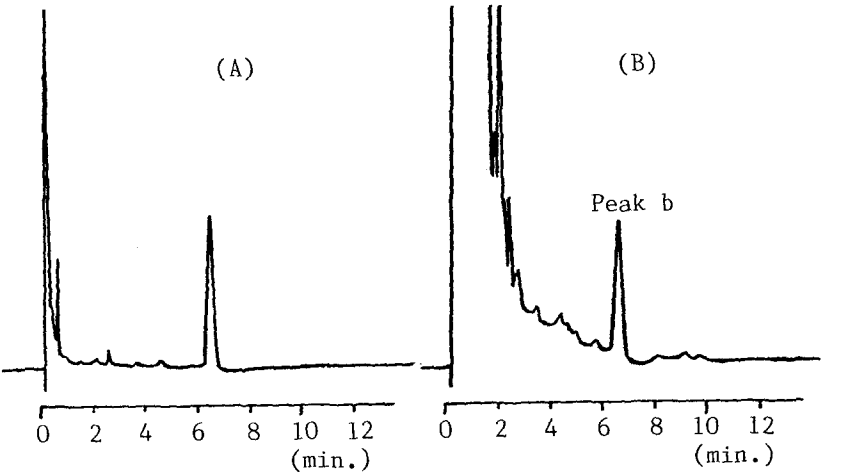

Figure 4. (A). Gas chromatogram of TBBP-DM standard.
(B). Gas chromatogram of the extract of mussel.

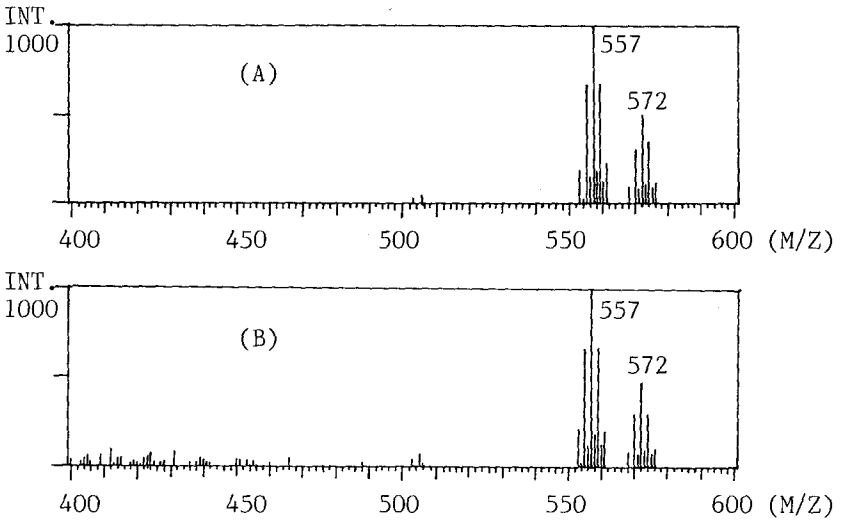

Figure 5. (A). Mass spectrum of TBBP-DM standard.
(B). Mass spectram of peak b in Fig. 4-(B).

formation since the chemical structure of TBBP is similar to that of pentachlorophenol.

Further investigations for the source of the TBBP pollution as well as metabolic and toxicological studies are required.

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