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### Identification of the flame retardant pentabromotoluene in sewage sludge

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Flame retardants constitute a rapidly growing sector of industrial chemicals<sup>1</sup>. These additives are very often polyhalogenated aromatics, very similar to polychlorinated biphenyls (PCBs) and hexachlorobenzene. Flame retardants may therefore be regarded as potential pollutants. An accident to cattle in Michigan, U.S.A., was recently reported to have been caused by the unintentional mixing of a flame retardant, hexabromobiphenyl, in the animal feed<sup>2-4</sup>. In this paper, we report on residues of pentabromotoluene (PBT) in sewage sludge. PBT is used as a flame retardant in textiles, polyester resins and paint emulsions.

The chromatographic examination of chlorinated hydrocarbons in a number of sewage sludge samples from Swedish waste-water treatment plants revealed three additional very large peaks in the sludge from one of the plants. These peaks covered much of the PCB spectrum. The substances were found to be very stable, not being decomposed by 7% fuming sulphuric acid or alkali. The compounds were identified by mass spectrometry as PBT and two isomers of tetrabromotoluene (TBT).

#### EXPERIMENTAL

Four samples of sewage sludge taken at different times from the same waste-water treatment plant were analyzed. Preliminary examinations were also carried out on fish, caught in the recipient near the outlet, and on soil and plants from a field manured with sludge about 5 months earlier. The product Flammex S-BT (Berk, London, Great Britain) was used as a reference. The quantitations are therefore only approximate.

The sewage sludge samples were originally analyzed for PCBs and other chlorinated hydrocarbons by using the following extraction procedure. To 5-10 g of the homogenized dried (60°) sample were added 50 ml of acetone and 25 ml of *n*-hexane. After mixing, the sample was allowed to stand overnight and the organic phase was then separated by adding 200 ml of 0.9% aqueous sodium chloride. A 15-ml aliquot of the hexane phase was evaporated under a flow of nitrogen. The residue was dissolv-

TABLE I  
RELATIVE RETENTION TIMES ( $p,p$ -DDE = 1.00) FOR BROMOTOLUENES DETERMINED BY GLC

Column No.	Column temperature ( $^{\circ}\text{C}$ )	Nitrogen flow-rate (ml/min)	TBT (I)	TBT (II)	PBT
I	195	26	0.35	0.42	1.07
II	195	23	0.34	0.41	1.05
III	185	19	0.42	0.47	1.24
IV	175	2*	0.39	0.43	1.31

\* Splitter outlet, 40 ml/min. Make-up gas to the electron capture detector, 20 ml/min.

ed in 4 ml of hexane and then shaken with 4 ml of 7% fuming sulphuric acid. After centrifugation, the hexane phase was separated and shaken with a drop of mercury and 2 ml of water. After additional centrifugation, 2–5  $\mu\text{l}$  of the hexane phase were injected into a gas chromatograph fitted with an electron capture detector. The method described is used by the National Swedish Laboratory for Agricultural Chemistry in routine analyses of PCBs and a number of chlorinated pesticides.

#### Gas-liquid chromatography (GLC)

A Varian (Palo Alto, Calif., U.S.A.) Model 2700 gas chromatograph with tritium electron capture detectors was used. Column temperatures and carrier gas flow-rates are given in Table I. The following columns were used. I: Pyrex, 3 m  $\times$  1.5 mm I.D. filled with 7.5% QF-1 + 5% OV-101 (3:1) on Chromosorb W, AW-DMCS, 100–120 mesh. II: Same as column I, but with a 15-cm pre-column containing 25% sodium hydroxide + 25% potassium hydroxide (1:1) on Chromosorb W, 100–120 mesh. III: Pyrex, 1.5 m  $\times$  1.5 mm I.D. filled with 5% OV-101 on Chromosorb W, AW-DMCS, 100–120 mesh. IV: Pyrex capillary column, ca. 50 m  $\times$  0.3 mm I.D., coated with SF-96.

#### Combined gas-liquid chromatography and mass spectrometry (GLC-MS)

A Pye Unicam (Cambridge, Great Britain) Model 84 gas chromatograph,

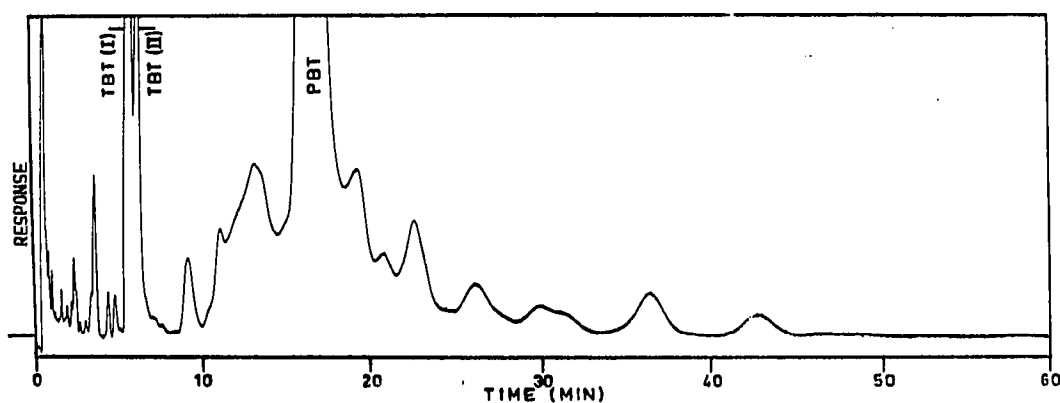


Fig. 1. Gas chromatogram of extract of sewage sludge sample A370 on column III.

**TABLE II**  
**SAMPLES ANALYZED FOR PENTABROMOTOLUENE**

<i>Sample</i>	<i>PBT</i> ( <i>mg/kg</i> )
Sewage sludge A370	~180
Sewage sludge A7	38
Sewage sludge A63	8
Sewage sludge A249	41
Soil	Trace (<0.1)
Barley, straw	Trace (<0.1)
Barley, grain	N.D.*
Oats, straw	N.D.*
Oats, grain	N.D.*
Fish, pike, muscle	N.D.*
Fish, pike, liver	N.D.*
Fish, perch, muscle	N.D.*
Fish, perch, liver	N.D.*

\* N.D. = not detected (<0.03 mg/kg).

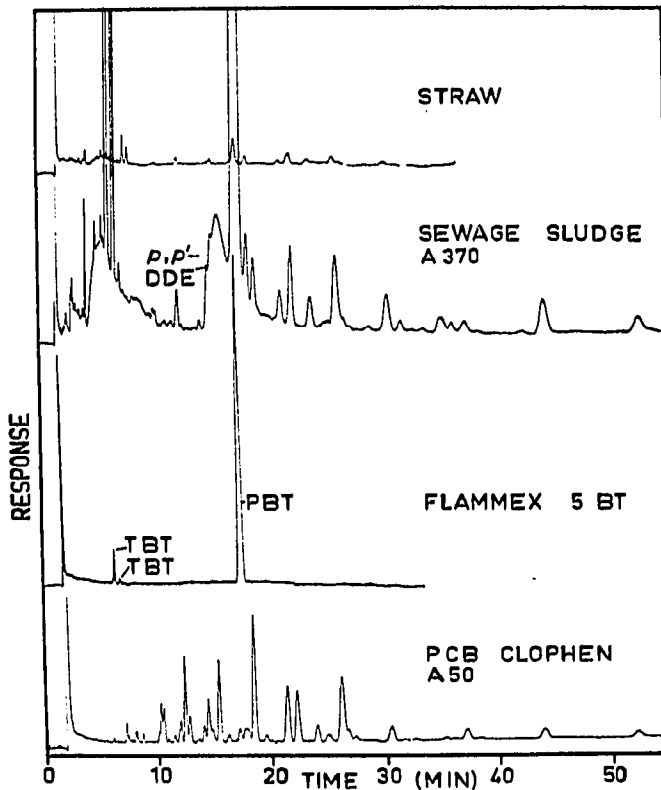


Fig. 2. Gas chromatograms of sample extracts, bromotoluenes and PCB separated on the glass capillary column.

fitted with a 1.5-m glass column filled with 1% OV-17 on Diatomite CQ, 100–120 mesh, was used. The operating parameters were as follows: injection block, 250°; column, 180°; detector oven, 300°; helium gas flow-rate, 30 ml/min. Part of the eluent gas passed into a flame ionization detector and the remainder into an LKB (Stockholm, Sweden) Model 9000 mass spectrometer. The connection between the gas chromatograph and the mass spectrometer was maintained at 200°, the separator at 220° and the ion source was operated at 70 eV and 270°. The GLC-MS system was connected with an on-line Multi-8 (Intertechnique) computer system (16K byte core memory) for sampling and processing of mass spectral data.

## RESULTS AND DISCUSSION

The extraction procedure described above is a routine method used for chlorinated hydrocarbon pollutants. No recovery experiments for the bromotoluenes have been carried out so far. The treatment with mercury serves to eliminate interfering sulphur and sulphur compounds from the extract<sup>5</sup>. Of the four columns used in the GLC identifications, columns I, II and III were packed columns, the first part of column II being filled with an alkaline packing. This pre-column is very useful for dirty extracts, and many interfering substances such as sulphur and its compounds are degraded there<sup>6</sup>. No degradation of penta- and tetrabromotoluene was observed in the pre-column. Column IV was a glass capillary column coated with SF-96 silicone oil on untreated Pyrex glass by a dynamic procedure. The sample was injected into

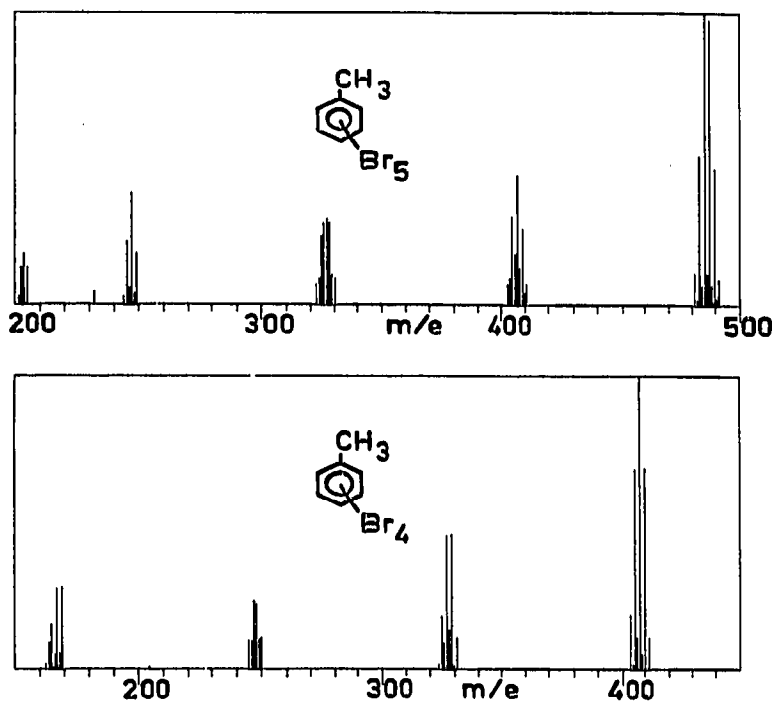


Fig. 3. Mass spectra of pentabromotoluene and tetrabromotoluene.

the column by a splitting technique. Relative retention times for the bromotoluenes on the four different columns are given in Table I. On columns I and II, PBT had a retention time very near to that of *p,p*-DDE, while on column III, it had a retention time very near to those of *p,p*-DDD and a large PCB peak. The capillary column separated PBT from DDT metabolites and large PCB peaks. Only a small PCB peak interfered (see Fig. 2). A chromatogram from the OV-101 column of the sewage sludge sample A370, extracted according to the above procedure, is shown in Fig. 1.

The results of the investigation are given in Table II, and Fig. 2 shows some chromatograms obtained using the capillary column (IV).

The mass spectral analyses were carried out at the Universities of Umeå and Stockholm. The spectra of PBT and one of the two TBT isomers are shown in Fig. 3. As the two TBT isomers gave identical spectra, it was not possible to distinguish between them. A comparison with the commercial flame retardant Flammex 5-BT (Berk) showed identical chromatographic and mass spectral behaviour. A factory using this waste-water treatment plant used Flammex 5-BT.

Metabolic studies have not yet been carried out, but it is intended to start such studies as soon as possible.

#### ACKNOWLEDGEMENT

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