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ANALYSIS OF POLYBROMINATED AROMATIC ETHERS

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SUMMARY

Commercially available polybrominated aromatic ethers, which are used as additive-type flame retardants, have been analysed by gas chromatography–mass spectrometry, high-performance liquid chromatography, reversed-phase thin-layer chromatography and UV spectrometry. For the polybrominated biphenyl ethers, the dependence of retention in the various chromatographic modes on bromine content, and the main substitution patterns, are discussed and compared with those for polybrominated biphenyls.

INTRODUCTION

Bromine-containing flame retardants have very diverse chemical structures[1]. According to Jenkner[2], in 1975 the production of bromine-containing compounds for application in plastics amounted to 28,000 tons in the U.S.A., Western Europe and Japan, and an annual growth rate of 15–17% has been predicted[1,2] for the near future.

In the literature, polybrominated aromatic ethers have received little attention from chemists and biologists. As far as polybrominated biphenyl ethers (PBBEs) (also called polybrominated diphenyl oxides) are concerned, Gersdorff and Schechter[3] have demonstrated the toxicity of 4-mono- and 4,4'-di-PBBE to house flies. Norris and co-workers[4–7] have made extensive investigations of the toxicological and environmental aspects of decabromobiphenyl ether (DBBE) prior to the marketing of this most widely used aromatic bromine-containing flame retardant. They concluded that DBBE offers a low risk in this respect following acute exposure. The main disadvantage of DBBE as additive to plastics is its low photostability[2,4], which is a well known characteristic of aromatic bromine compounds. Japanese manufacturers solved this problem by replacing one or more of the bromine atoms in the *ortho* position to the ether linkage with hydrogen[8,9]. Sundström and Hutzinger[10] identified 2,4,2',4'-tetra- and 2,4,5,2',4'-penta-PBBE as the major components of Bromkal 70-5 DE.

Norström et al.[11] reported the main constituents of some commercially

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available mixtures of brominated biphenyl, alkyl phenyl and allyl phenyl ethers. The fungistatic activity and toxicity of the latter types of ethers were investigated by Felton and MacLaughlin[12]. Recently, Erickson et al.[13] detected trace amounts of a chlorine-containing ether ($C_{12}Br_9ClO$) in several commercial samples of DBBE. Some further information concerning the brominated aromatic ethers can be obtained from patents[14,15] and technical bulletins[16,17]. To our knowledge, PBBEs and other such ethers have not been detected in the environment. However, trace amounts of the closely related polychlorinated biphenyl ethers have been identified in technically produced chlorinated phenols, mainly those with three or more chlorine substituents[18,19].

In this paper, we describe the analysis of polybrominated aromatic ethers, especially PBBEs, by chromatographic and spectrometric techniques.

EXPERIMENTAL

Materials

Biphenyl ether (Schuchardt, zur Synthese) was purchased from Merck (Darmstadt, G.F.R.). Another sample of this ether was obtained as a gift from I.S.C. Chemicals (Bristol, Great Britain), who also supplied us with samples of the commercially produced PBBE mixtures Tardex 50, 80 and 100. Samples of the PBBE mixtures Bromkal 70-5 DE, 79-8 DE and 82-0 DE and of the brominated allyl phenyl and propyl phenyl ether mixtures Bromkal 64-3 AE, 74-5 AE and 73-5 PE were received as gifts from Chemische Fabrik Kalk (Cologne, G.F.R.).

All samples were homogenized before use. Sample solutions were prepared in tetrachloromethane [for high-performance liquid chromatography (HPLC) and gas chromatography (GC)] or n-hexane [for thin-layer chromatography (TLC) and ultraviolet (UV) spectrometry]. In order to prevent photodegradation of the samples in the solid or dissolved state, all bottles were wrapped in aluminium foil and stored in a refrigerator.

Methods

HPLC was carried out in the system silica gel (LiChrosorb SI-60)–dry n-hexane at a temperature of $27 \pm 1°$, using UV detection. Reversed-phase TLC was performed in the system Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–acetone–water (20:20:9:1), using a length of run of 16 cm; identification was effected by spraying with a solution of tolidine in ethanol and subsequent irradiation with UV light.

Gas chromatograms were run using glass columns packed with 1% SE-30 or 2% OV-17 on Chromosorb W HP and W AW DMCS, respectively, using flame-ionization detection.

For GC–mass spectrometry (MS), a gas chromatograph connected with a quadrupole mass spectrometer with electron impact at 70 eV and a source temperature of 230° was used.

Details of all of these procedures, apparatus and chemicals have been reported previously[20]. For the more highly brominated samples, GC–MS was performed on a JEOL JGC-20K gas chromatograph connected with a double-focusing JEOL JMS-D 100 mass spectrometer (JEOL, Tokyo, Japan) with electron impact at 70 eV and a

source temperature of 280°; the temperature of the separator was maintained at 300°. [1]H Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker WH 90 F.T. spectrometer (Bruker-Physik, Karlsruhe, G.F.R.).

RESULTS AND DISCUSSION

Biphenyl ether

Both samples of biphenyl ether had a purity of over 99%. The UV spectrum of this compound, which is the starting material for the synthesis of PBBEs, is shown in Fig. 1. At the wavelengths of maximal absorption (197 and 226 nm), $\log \varepsilon = 4.50$ and 4.00, respectively.
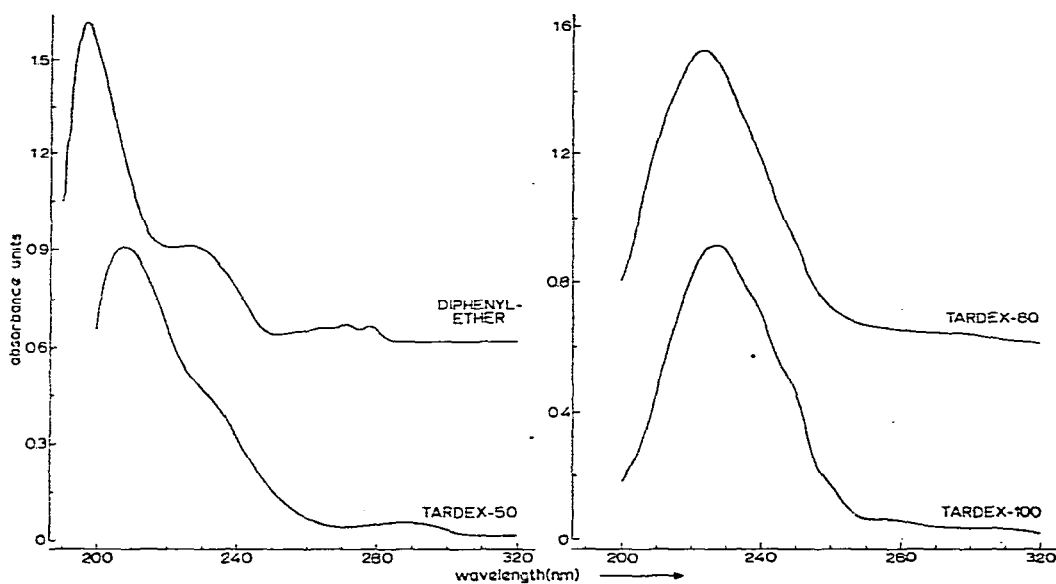

Fig. 1. UV absorption spectra of biphenyl ether and Tardex 50, 80 and 100. Concentrations: 40, 66, 78 and 120 ppm, respectively, in n-hexane. Cell path length, 2 mm.

Polybrominated alkyl phenyl and allyl phenyl ethers

Table I summarizes analytical data on the polybrominated alkyl phenyl and allyl phenyl ethers taken from the literature. UV spectral characteristics for the crude samples and HPLC and GC retention data for the main component present in each sample are given in Table II. The UV spectra are rather similar to those recorded for polybrominated biphenyls (PBBs) and PBBEs, which will be discussed in more detail below.

Assuming equal responses for the main component and any impurities present, purities of 96% and 99% were calculated for Bromkal 73-5 PE and 64-3 AE, respectively; Bromkal 74-5 AE was less pure (cf., Table II). GC–MS and ^{1}H NMR spectrometry showed the main constituents of these mixtures to be 2,3-dibromopropyl 2,4,6-tribromophenyl ether, allyl 2,4,6-tribromophenyl ether and allyl pentabromophenyl ether, respectively. This confirms the assignments given by the manufacturer[16]. The second largest peak in Bromkal 74-5 AE ($t_{R,GC} = 8.2$ min), which is also a trace

TABLE I

SURVEY OF LITERATURE DATA ON THE ANALYSIS OF POLYBROMINATED ALKYL PHENYL AND ALLYL PHENYL ETHER MIXTURES

Brominated ether mixture	Manu-facturer*	Wt.-% of Br	Melting-point range (°C)	Specific gravity	Main component(s)	Refer-ence
Bromkal 64-3 AE	K	63–65	74–77	2.2	Allyl 2,4,6-tribromophenyl ether	16
Bromkal 74-5 AE	K	74–75	160–165	2.7	Allyl pentabromophenyl ether	16
Bromkal 73-5 PE	K	73–75	40	2.3	2,3-Dibromopropyl 2,4,6-tri-bromophenyl ether	16
Flammex 5 AE	B.				93% of allyl pentabromophenyl ether; 7% (2 isomers) of tetrabromo compounds	11

* K = Chemische Fabrik Kalk (Cologne, G.F.R.); B = Berk (London, Great Britain).

component of Bromkal 64-3 AE, was shown to be an allyl tetrabromophenyl ether. It is interesting that Bromkal 73-5 PE is a brominated propyl phenyl ether, as Norström et al.[11] showed that the so-called Pentabromprop (Kalk product), claimed to be a dibromopropyl tribromophenyl ether, is actually a mixture of mainly tetra- and pentabromo biphenyl ethers.

Polybrominated biphenyl ethers

Literature data on the composition and analysis of PBBE mixtures are reported in Table III. This table reveals that, apart from information provided by the manu-facturers, there is a lack of information for all mixtures. Table IV summarizes UV spectral characteristics and data on the composition of the crude samples; retention data for HPLC and GC can be seen in Fig. 2 (see below).

UV spectrometry. The UV absorption spectra of biphenyl ether and a few low-brominated (2-, 4-, 4,4'- and 2,4,4'-) PBBEs have been studied by several groups of workers[22–25]. Their main conclusion was that the introduction of bromine atoms into the biphenyl ether nucleus in the positions indicated above does not materially modify the absorption curve of the parent compound. This agrees with the recent conclusion of Choudry et al.[26], who stated that the introduction of one or two sub-

TABLE II

CHARACTERISTICS OF POLYBROMINATED ALKYL PHENYL AND ALLYL PHENYL ETHER MIXTURES

HPLC: LiChrosorb SI-60–dry n-hexane; flow-rate, 1.4 ml·min^{-1}; UV detection at $\lambda_{max.}$; $k' = (t_R - t_0)/t_0$. GC: 1% SE-30 on Chromosorb W HP; flow-rate (He), 30 ml·min^{-1}; column temperature, 160°; flame-ionization detection.

Brominated ether mixture	Main band		Wt.-%			Main component		Remarks
	$\lambda_{max.}$ (nm)	$\log \varepsilon$ ($l·mole^{-1}·cm^{-1}$)	Br_5	Br_4	Br_3	k'_{LC}	$t_{R.GC}$ (min)	
Bromkal 64-3 AE	212	4.73	—	—	99	6.70	2.70	3 trace components
Bromkal 74-5 AE	224	4.70	81	12	—	3.05	27.5	3% pentabromophenol
Bromkal 73-5 PE	212	4.72	96	—	—	10.50	23.3	2 more components (3+1%)

TABLE III

SURVEY OF LITERATURE DATA ON THE ANALYSIS OF POLYBROMINATED BIPHENYL ETHER MIXTURES

Brominated ether mixture	Manufacturer*	Wt.-% Br	Melting-point range (°C)	Br_{10}	Br_9	Br_8	Br_7	Br_6	Br_5	Br_4	Remarks***	Ref.
PBBEs												
Pentabromprop	K	—	—	—	—	—	—	9 (2)	61 (3)	39 (4)	one m Br_5, one m Br_4	11
Bronkal 70-5 DE	K	67-71	—	—	—	—	0.2	5.8	59.8	34.2		2, 16
Bronkal 70-5 DE	K	—	—	—	—	—	—	—	45 (2)	41.7 (1)	$Br_4 = 2,4,2',4'$-; m $Br_5 = 2,4,5,2',4'$-	10
Bronkal 70	K	—	—	—	—	—	—	—	74 (2)	36	one m Br_5; m $Br_4 = 2,4,2',4'$-	11
Pentabromodiphenyl oxide	I	71.8	—	—	—	—	—	—	58	35	4% Br_x (x > 5)	14
Bronkal 79-8 DE	K	79-80	170-220	—	—	—	—	—	—	—	m = Br_8	16
Octabromobiphenyl ether	K	—	—	—	t	34 (2)	62	4 (2)	—	—		2, 11
Bronkal 82-0 DE	K	82-83	290-310	92.9	1.8	5.0	0.3	—	—	—	m = Br_{10}	2, 16
DBBEs												
—	M	83.42	—	—	—	—	—	—	—	—	1.79% oxygen	15
HFO 102	H	—	304	—	—	—	—	—	—	—		17
FR-300	D	83	290-306	77.4	21.8 (2)	0.8	—	—	—	—		4, 6
—	1	—	—	94.6	5.2	0.2	—	—	—	—		21

* Manufacturers: K = Chemische Fabrik Kalk (Cologne, G.F.R.); I = I.S.C. Chemicals (Bristol, Great Britain); M = Michigan Chem. Corp. (Michigan, Ill., U.S.A.); H = Hexcel (Basildon, Great Britain); D = Dow Chemical (Midland, Mich., U.S.A.).

** No. of isomers in parentheses; t = trace.

*** m = major components.

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TABLE IV

COMPOSITION AND SPECTRAL CHARACTERISTICS OF POLYBROMINATED BIPHENYL ETHER MIXTURES

Sample	Main band		Wt.-%[*]						
	$\lambda_{max.}$ (nm)	log ε ($l \cdot mole^{-1} \cdot cm^{-1}$)	Br_{10}	Br_9	Br_8	Br_7	Br_6	Br_5	Br_4
Bromkal 70-5 DE	205	4.78				(2)	7 (2)	55 (3)[**]	38 (1)
Tardex 50	208	4.75				1 (1)	13 (2)[**]	60 (3)[**]	26 (1)
Bromkal 79-8 DE	224	4.87	19	46 (2)[**]	26 (2)[**]	8 (1)			
Tardex 80	224	4.86	23	41 (2)[**]	28 (2)[**]	7 (1)			
Bromkal 82-0 DE	228	5.18	86	12 (3?)[**]	0.1 (2)				
Tardex 100	228	4.73	92	8 (3?)	0.1 (2)				

    [*] No. of isomers in parentheses.
  [**] Denotes the presence of one distinctly major isomer.

stituents in the positions *ortho* to the C–O–C moiety does not decrease the molar extinction coefficients (or alter the wavelengths) of the absorption maxima of chlorinated biphenyl ethers around 270–280 nm. However, with more highly halogenated ethers, *ortho* substitution obviously does play a role; that is, it interferes with conjugation through the C–O–C moiety, as shown by the gradual disappearance of the absorption maxima in the 260–300 nm range when going from biphenyl ether to Tardex 100 (Fig. 1). Our observation agrees with those previously reported for halogenated biphenyls[20,27], and this also holds for the fact that the main absorption maximum, occurring at 197 nm for biphenyl ether, shows a distinct shift to longer wavelengths with increasing bromine substitution.

Gas chromatography. Gas chromatograms of the complete Bromkal PBBE series are shown in Fig. 2. As with PBBs, excellent resolution is obtained for these mixtures, with either 1 % SE-30 or 2 % OV-17 as the stationary phase. Sundström and Hutzinger[10] and Norström *et al.*[11] demonstrated the presence of one tetrabromo- and two pentabromobiphenyl ethers in Bromkal 70-5 DE, ¹H NMR spectrometry showing the main constituents to be 2,4,2′,4′-tetra- and 2,4,5,2′,4′-penta-PBBE. The present results extend the earlier reports by indicating the bromine numbers of six minor components. Peaks were identified by means of their mass-fragmentation patterns, which are analogous to those for polychlorinated biphenyl ethers[18,19], *e.g.*, subsequent loss of halogen atoms and halogen(s) plus carbon monoxide from the molecular ion. The elimination of carbon monoxide is a well known phenomenon with substituted biphenyl ethers[28,29].

On the basis of the UV, GC and GC–MS data, we can conclude that Tardex 50 and Bromkal 70-5 DE have similar compositions, even though the former mixture contains distinctly less of the tetra isomer and about twice as much of the main hexa-substituted PBBE (6″ in Fig. 2). Our results agree satisfactorily with those published by Jenkner[2], Belf[14] and the manufacturer[16]. On the other hand, they deviate markedly from the data (on the pentabromo content) reported in refs. 10 and 11. However, as regards the latter paper, one should probably read "64" instead of "74" for the weight percentage of pentabromo isomers, as the tetrabromo percentage is given as 36. In view of the analogy observed between the bromination, *i.e.*, the substitution pattern, of biphenyl and biphenyl ether[10] and the fact that 2,4,5,2′,4′,5′-

Fig. 2. GC and HPLC of Bromkal 70-5 DE, 79-8 DE and 82-0 DE. GC: 1 % SE-30 on Chromosorb W HP; column temperature, 240° (Bromkal 70-5 DE) or 280° (other Bromkals); flow-rate (helium), 30 ml·min⁻¹. HPLC: LiChrosorb SI-60–dry n-hexane; flow-rate, 1.4 ml·min⁻¹; UV detection at 225 nm; temperature, 27 ± 1°. Numbers above the peaks designate the number of bromine atoms per PBBE molecule. A–C denote fractions collected in HPLC and analysed by GC; * and ** indicate 2,4,2′,4′-tetra- and 2,4,5,2′,4′-pentabromobiphenyl ether, respectively (see text).

hexabromobiphenyl has been shown[20,30,31] unequivocally to be the main component of fireMaster BP-6, it seems justified to predict 2,4,5,2',4',5'-hexabromo-PBBE as the structure of the main hexa isomer in Tardex 50 and Bromkal 70-5 DE.

The similar compositions of Bromkal and Tardex mixtures noted above was also observed from Bromkal 79-8 DE and Tardex 80. The only major difference is that the main octa isomer in the Bromkal mixture is a minor constituent in Tardex 80. According to the manufacturer[16], the main component of Bromkal 79-8 DE is octabromobiphenyl ether; in view of the results of the present analyses, this is difficult to understand. We should add that "Octabromobiphenyl ether", another Kalk product, analysed by Norström et al.[11], in all probability had a composition distinctly different from that of the present sample, as shown by the fact that a hepta-substituted PBBE was the main component and that only trace amounts of nona isomers were detected.

Both Bromkal 82-0 DE and Tardex 100 are about 90% pure DBBE preparations, containing nona isomers as principal contaminants. In view of the closely analogous composition of these two technical mixtures, it is surprising that our results differ considerably from those reported by Jenkner[2] regarding the percentages of nona- and octa-substituted PBBEs. For the remainder, it can be seen in Fig. 2 that trace amounts of all octa- and nona-substituted PBBEs observed in Bromkal 79-8 DE occur in Bromkal 82-0 DE. For the highly brominated PBBE mixtures, the similarity in the substitution patterns of biphenyl and biphenyl ether referred to above can be used to predict the structure of the main nona isomer. Recently, the main nona isomer present in the PBB mixtures Bromkal 80-9 D and "Octabromobiphenyl" has been shown[32] unambiguously to be 2,3,4,5,6,2',3',4',5'-nona-PBB; consequently, the main isomer in the PBBE mixtures is probably 2,3,4,5,6,2',3',4',5'-nona-PBBE. Here, it is interesting to note that Norris et al.[4], who studied the photodegradation of DBBE in xylene, reported that during the first 5–7 h of exposure to irradiation, the weight percentage of one nona isomer increases distinctly more rapidly than that of the other one originally present in the sample. Now, as debromination at positions *ortho* to the central C–C bond is the preferred route of degradation of PBBs in non-polar solvents[32-34], one can expect similar behaviour for PBBEs and, thus, DBBE (*cf.*, refs. 8 and 9). In other words, the faster "growing" isomer is 2,3,4,5,6,2',3',4',5'-nona-PBBE.

Liquid chromatography. Chromatograms of the Bromkal PBBE series in the system silica gel–dry *n*-hexane are included in Fig. 2. In order to permit the assignment of bromine numbers to the main peaks in the HPLC chromatograms, several fractionation experiments were run. Fractions A, B and C as indicated in Fig. 2 were collected in amounts sufficient to allow their analysis by GC. The results, which are shown in Fig. 2, indicate that the identification of the main peaks was successful in all instances.

Further, one can conclude that the resolution of the relatively polar highly brominated PBBEs is superior to that of the corresponding PBBs: for PBBs, only a single peak was observed[20] in the HPLC of all mixtures chiefly containing octa- and/or higher brominated components. Also, as is to be expected on the basis of results previously obtained for halogenated biphenyls and naphthalenes, the retention of the PBBEs depends on both the number and position of the bromine atoms in the biphenyl ether nucleus: retention tends to decrease with an increasing number of substituents, but this rule is not strictly adhered to.

Finally, the behaviour of two Bromkal mixtures in reversed-phase TLC was studied (Fig. 3). GC analysis of the various TLC fractions enabled us to establish the bromine numbers of the zone components, as indicated in Fig. 3. With Bromkal 70-5 DE, HPLC analysis of the fractions confirmed the results obtained by means of GC. It is noteworthy that again the separation of the PBBEs is much better than that of highly brominated PBB mixtures, the Bromkal 80-9 D referred to above showing only two (contiguous) zones. In addition, the R_F values of the PBBEs appear to depend considerably on the number of bromine substituents. The sharp separations obtained in reversed-phase TLC suggest that HPLC on a non-polar bonded-phase packing might be competitive with GC. Preliminary experiments in our laboratory confirmed this possibility: at least five cleanly separated peaks were found in a chromatogram of Bromkal 79-8 DE run in the system LiChrosorb RP-8–methanol containing 10–15% of water.
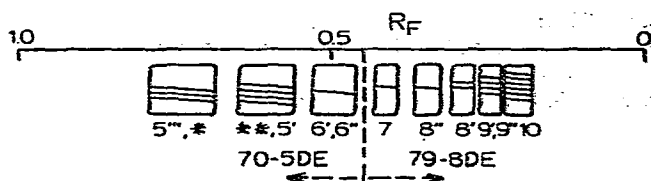

Fig. 3. TLC of Bromkal 70-5 DE and 79-8 DE in the system Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–acetone–water (20:20:9:1); length of run, 16 cm. Asterisks as in Fig. 2.

REFERENCES

1 R. Liepins and E. M. Pearce, *Environ. Health Perspect.*, 17 (1976) 55.
2 H. Jenkner, *Plaste Kautsch.*, 24 (1977) 415.
3 W. A. Gersdorff and M. S. Schechter, *Soap Sanit. Chem.*, 24 (1948) 155.
4 J. M. Norris, J. W. Ehrmantraut, C. L. Gibbons, R. J. Kociba, B. A. Schwetz, J. Q. Rose, C. G. Humiston, G. L. Jewett, W. B. Crummett, P. J. Gehring, J. B. Tirsell and J. S. Brosier, *J. Fire Flamm. Combust. Toxicol.*, 1 (1974) 52.
5 R. J. Kociba, L. O. Frauson, C. G. Humiston, J. M. Norris, C. E. Wade, R. W. Lisowe, J. F. Quast, G. C. Jersey and G. L. Jewett, *J. Fire Flamm. Combust. Toxicol.*, 2 (1975) 267.
6 J. M. Norris, R. J. Kociba, B. A. Schwetz, J. Q. Rose, C. G. Humiston, G. L. Jewett, P. J. Gehring and J. B. Mailhes, *Environ. Health Perspect.*, 11 (1975) 153.
7 J. M. Norris, R. J. Kociba, B. A. Schwetz, J. Q. Rose, C. G. Humiston and P. J. Gehring, *Pharmacologist*, 15 (1973) 394.
8 Y. Noguchi, E. Noda and K. Toyoshima, *Japan Kokai*, No. 76,128,929 (1976).
9 Y. Noguchi, E. Noda and K. Toyoshima, *Japan Kokai*, No. 76,128,928 (1976).
10 G. Sundström and O. Hutzinger, *Chemosphere*, 5 (1976) 187.
11 A. Norström, K. Andersson and C. Rappe, *Chemosphere*, 5 (1976) 255.
12 L. C. Felton and B. MacLaughlin, *J. Org. Chem.*, 12 (1947) 298.
13 M. D. Erickson, R. A. Zweidinger and E. D. Pellizzari, *Analysis of a Series of Samples for PBBs*, EPA-560/6-77-020, Office of Toxic Substances, Washington, D.C., 1977.
14 L. J. Belf, *Brit. Pat.*, No. 1,436,657 (1976).
15 H. Stepniczka, *U.S. Pat.*, No. 3,965,197 (1976).

16 *Flammschutzmittel für Kunststoffe*, Chemische Fabrik Kalk, Cologne, G.F.R.
17 *Flame Retardants Product Summary*, Hexcel, Basildon, Great Britain.
18 D. Firestone, J. Ress, N. L. Brown, R. P. Barron and J. N. Damico, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 85.
19 H.-R. Buser, *J. Chromatogr.*, 107 (1975) 295.
20 J. J. de Kok, A. de Kok, U. A. Th. Brinkman and R. M. Kok, *J. Chromatogr.*, 142 (1977) 367.
21 L. J. Belf, *Brit. Pat.*, No. 1,472,383 (1975).
22 R. Passerini and G. Righi, *Boll. Sci. Fac. Chim. Ind. Bologna*, 10 (1952) 163.
23 R. Passerini and G. Righi, *Boll. Sci. Fac. Chim. Ind. Bologna*, 10 (1952) 166.
24 A. Cerniani, R. Passerini and G. Righi, *Boll. Sci. Fac. Chim. Ind. Bologna*, 12 (1954) 114.
25 M. Dahlgard and R. Q. Brewster, *J. Amer. Chem. Soc.*, 80 (1958) 5861.
26 G. G. Choudry, G. Sundström, L. O. Ruzo and O. Hutzinger, *J. Agr. Food Chem.*, 25 (1977) 1371.
27 U. A. Th. Brinkman, J. W. F. L. Seetz and H. G. M. Reymer, *J. Chromatogr.*, 116 (1976) 353.
28 R. G. Cooks, R. S. Ward, I. Howe and D. H. Williams, *Chem. Commun.*, (1968) 837.
29 I. Granoth, *J. Chem. Soc., Perkin II*, (1972) 1503.
30 K. Andersson, A. Norström, C. Rappe, B. Rasmuson and H. Swahlin, *Environ. Qual. Saf.*, Suppl. Vol. III (1975) 798.
31 G. Sundström, O. Hutzinger and S Safe, *Chemosphere*, 5 (1976) 11.
32 J. J. de Kok, A. de Kok, J. van der Giessen and U. A. Th. Brinkman, in preparation.
33 D. R. Erney, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 1202.
34 L. O. Ruzo, G. Sundström, O. Hutzinger and S. Safe, *J. Agr. Food Chem.*, 24 (1976) 1062.