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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XLIX[a]. POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS ON LOW-POLARITY NB-54 AND NB-1701 CAPILLARY COLUMNS

ILPO O. O. KORHONEN* and KEIJO M. MÄNTYKOSKI
Department of Chemistry, University of Jyväskylä, Tellervonkatu 8, SF-40100 Jyväskylä 10 (Finland)
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SUMMARY

The gas chromatographic retention behaviour of complex mixtures of sixteen polychlorinated dibenzo-*p*-dioxins and fourteen polychlorinated dibenzofurans, containing in addition to the most toxic 2,3,7,8-chloro isomers the so-called "window" isomers, was studied on low-polarity NB-54 and NB-1701 capillary columns under suitable temperature-programmed conditions. The retention data for the components are given and their separation is discussed. The results are compared with those of the related isomers reported previously on low-polarity and polar stationary phases.

INTRODUCTION

Many papers have been published in the last 10 years on analytical methods for polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in various biological and environmental samples[1–8]. After clean-up procedures the final analyses were performed by gas chromatography (GC) with electron-capture detection (ECD) and frequently with mass-selective detection. Packed and capillary columns with low-polarity or polar stationary phases as listed in Table I[9–58] have been used separating the individual components from complex mixtures. Isomers, their concentration levels, total amounts and relative recoveries, etc., have been widely reported, but relatively few publications[9,11–17,20,25,31–33,38] seem to give the exact retention data for compounds, however, although the chromatograms were shown.

As a continuation of our research on harmful organochlorine compounds in the environment[59], this paper reports the GC retention behaviour of several PCDDs and PCDFs on capillary columns coated with low-polarity NB-54 and NB-1701 stationary phases. The mixtures were analysed using a double-column system with suitable temperature programming. The relative retention data are given, the results being compared with those reported previously for related isomers.

[a] For Part XLVIII, see I. O. O. Korhonen, *J. Chromatogr.*, 363 (1986) 277.

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TABLE I

STATIONARY PHASES USED FOR GC SEPARATION OF PCDD AND/OR PCDF COMPOUNDS

This is not a complete list, but it contains the most important phases.

Stationary phase	*Refs.*	*Stationary phase*	*Refs.*
C-87	25	OV-101	2, 10, 27, 34
Carbowax 20M	2, 9	OV-105	2
CPS-2	10	OV-210	2
Cyanopropyltolylallylsiloxane	11	OV-225	2, 27
DB-5	10, 12–24	OV-240-OH	35
DB-17	25, 26	OV-1701	28, 33
DB-1701	25	SB smectic	36, 37
Dexil 300	2	SE-54	2, 10, 15, 33, 38–42
Dexil 410	27	Sil-88	21, 37, 43
Methylsilicone	2, 28, 29	Silar 10C	2, 25, 31, 44–47
OV-1	2, 27, 28, 30–33	SP-2100	2, 48
OV-3	2	SP-2330	10, 15, 19, 20, 25, 28, 30, 32, 49–54
OV-7	2	SP-2331	6, 16, 26, 50, 55–57
OV-17	2, 12, 34	SP-2340	10, 58
OV-17/Poly S-179	2	SP-2350	58
OV-61	2	XE-60	2

EXPERIMENTAL

Materials

All 2,3,7,8-substituted PCDDs (2, 6, 10–12, 15 and 16) and PCDFs (18, 21, 22, 25–27, 29 and 30) were obtained from Wellington Labs. (Ontario, Canada) and the other isomers (1, 3–5, 7–9, 13, 14, 17, 19, 20, 23, 24 and 28) from CIL (Cambridge Isotope Labs., MA, U.S.A.). The mixtures analysed contained suitable amounts of the individual components for the sensitivity of the electron-capture detector.

Methods

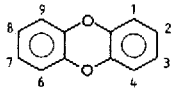
GC analyses were carried out on a Nordion Micromat HRGC 412 gas chromatograph under the following operating conditions: injection and electron-capture detector temperatures, 275 and 320°C, respectively; helium carrier gas velocity, 32 cm min^{-1}; and chart speed, 10 mm min^{-1}. A double-column system was used with the following low-polarity columns: a fused-silica NB-54 (5% phenyl-, 1% vinylmethylsilicone, similar to SE-54) wall-coated open-tubular (WCOT) column (25 m × 0.32 mm I.D., film thickness 25 μm) and a fused-silica NB-1701 (7% phenyl-, 7% cyanopropylmethylsilicone, similar to OV-1701) WCOT column (25 m × 0.32 mm I.D., film thickness 25 μm), both supplied by HNU-Nordion (Helsinki, Finland). The oven temperature was held at 100°C for 1 min, then programmed to 180°C at 20°C min^{-1} and from 180 to 280°C at 5°C min^{-1}, and held at the final temperature until elution of peaks had ceased. Both columns were operated simultaneously.

The chromatographic data were recorded with a Trendcom Synnyvale Model 200 integrator using standard programs, the retention times being measured from the time of sample injection.

TABLE II

RETENTION DATA FOR POLYCHLORINATED DIBENZO-*p*-DIOXINS OBTAINED ON NB-54 AND NB-1701 CAPILLARY COLUMNS

Conditions as in Fig. 1.



Peak No.	*Systematic No.*[a]	*Compound*[b]	*Column*				
			NB-54		*NB-1701*		
			ART[c]	*RRT*[d]	*ART*[c]	*RRT*[d]	*RRT*[e]
1	42	1,3,6,8	19.50	0.919	20.62	0.911	1.057
2	48	2,3,7,8	21.21	1.000	22.63	1.000	1.067
3	41	1,2,8,9	21.94	1.034	24.11	1.065	1.099
4	58	1,2,4,6,8	23.21	1.094	24.61	1.087	1.060
5	61	1,2,4,7,9	23.21	1.094	24.61	1.087	1.060
6	54	1,2,3,7,8	24.80	1.169	26.40	1.167	1.065
7	56	1,2,3,8,9	25.22	1.189	27.39	1.210	1.086
8	71	1,2,4,6,7,9	26.89	1.268	29.02	1.282	1.079
9	72	1,2,4,6,8,9	26.89	1.268	29.02	1.282	1.079
10	66	1,2,3,4,7,8	28.48	1.343	30.77	1.360	1.080
11	67	1,2,3,6,7,8	28.60	1.348	30.92	1.366	1.081
12	70	1,2,3,7,8,9	29.00	1.367	31.72	1.402	1.094
13	63	1,2,3,4,6,7	29.05	1.370	31.90	1.410	1.098
14	74	1,2,3,4,6,7,9	32.53	1.534	36.20	1.600	1.113
15	73	1,2,3,4,6,7,8	34.03	1.604	37.91	1.675	1.114
16	75	1,2,3,4,6,7,8,9	41.44	1.954	48.02	2.122	1.159

[a] Taken from ref. 60.
[b] Numbers indicate the chlorinated positions.
[c] Absolute retention times (min) were measured from sample injection (Fig. 1).
[d] Relative retention time for 2 taken as 1.000.
[e] Relative retention time for the corresponding isomer on NB-54 taken as 1.000.

RESULTS AND DISCUSSION

PCDDs

Chromatograms of a mixture of PCDDs (1–16) are illustrated in Fig. 1 and Table II gives the corresponding retention data.

As would be expected, the individual components are eluted on the low-polarity columns used in the order corresponding to their degree of chlorination, *i.e.*, tetra- < penta- < hexa- < hepta- < octachloro isomers. The so-called "window" isomers for low-polarity phases, *viz.*, the first and last isomer eluting in each group, are then 1 and 3 for tetra-, 4 + 5 and 7 for penta- and 8 + 9 and 13 for hexachloro PCDDs, respectively (Fig. 1). Based on earlier observations[14,15,17,31,32], the deficient isomers not investigated in this work elute between these "window" isomers.

On NB-54, a mixture of sixteen components shows 13 resolved peaks, so that 4 and 5, 8 and 9, and 12 and 13 overlapped and 10 and 11 are partially separated from

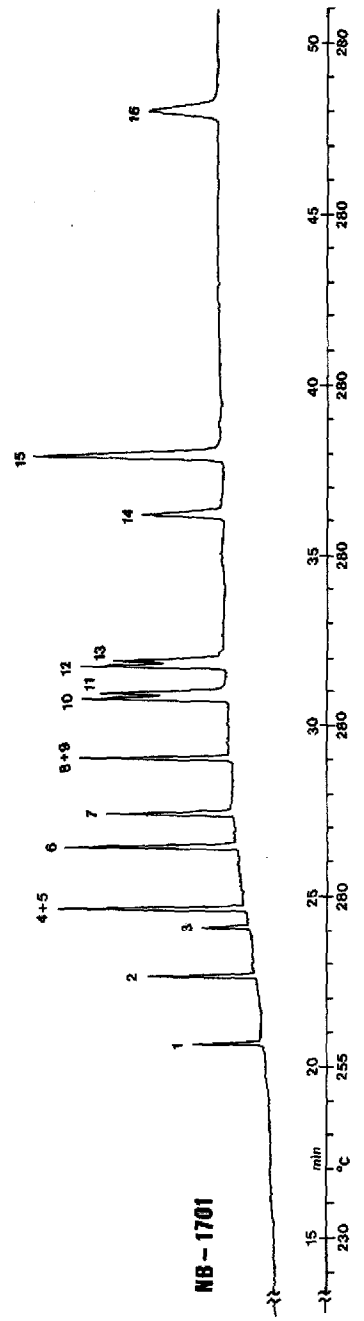


Fig. 1. Chromatogram of a mixture of polychlorinated dibenzo-*p*-dioxins (PCDDs), separated on low-polarity NB-54 and NB-1701 capillary columns with the following temperature programme: initial 1 min at 100°C, 100 to 180°C at 20°C min^{-1}, 180 to 280°C at 5°C min^{-1}, held at 280°C until elution of peaks had ceased. Peaks 1–16 are identified in Table II.

each other. With increasing column polarity, *i.e.*, on NB-1701 the retention of the isomers increases (Table II), as expected, the mixture giving 14 resolved peaks (Fig. 1). The retention order between the isomers remains unchanged. Compounds 4 and 5, and 8 and 9 are again coincident, whereas 12 and 13 show partially separated peaks like 10 and 11. The separation of the latter pair would have been expected to be better with a higher column polarity. However, earlier results with polar Silar 10C[46,47] and SP-2330[6] capillary columns showed only a slightly better separation between 10 and 11. Isomers 4 and 5, and 8 and 9 are also coincident on these phases, whereas 12 and 13 are completely separated.

The results obtained are in good agreement with the calculated and measured values reported previously on a low-polarity DB-5[17] capillary column and in contradiction to the elution order of the pair 10 and 11, obtained earlier on low-polarity SE-54 and OV-1701 capillary columns[33]. Hence, it seems evident that the retention order of isomers on these columns would also be the same as in the present investigation, particularly owing to the almost identical stationary phases and the fact that retention order of PCDDs is shown to be apparently constant with different low-polarity and slightly polar phases[17].

PCDFs

Generally the same trends as above are found also with the mixture of PCDFs (17–30) (Fig. 2 and Table III). The separation is nearly complete on both stationary

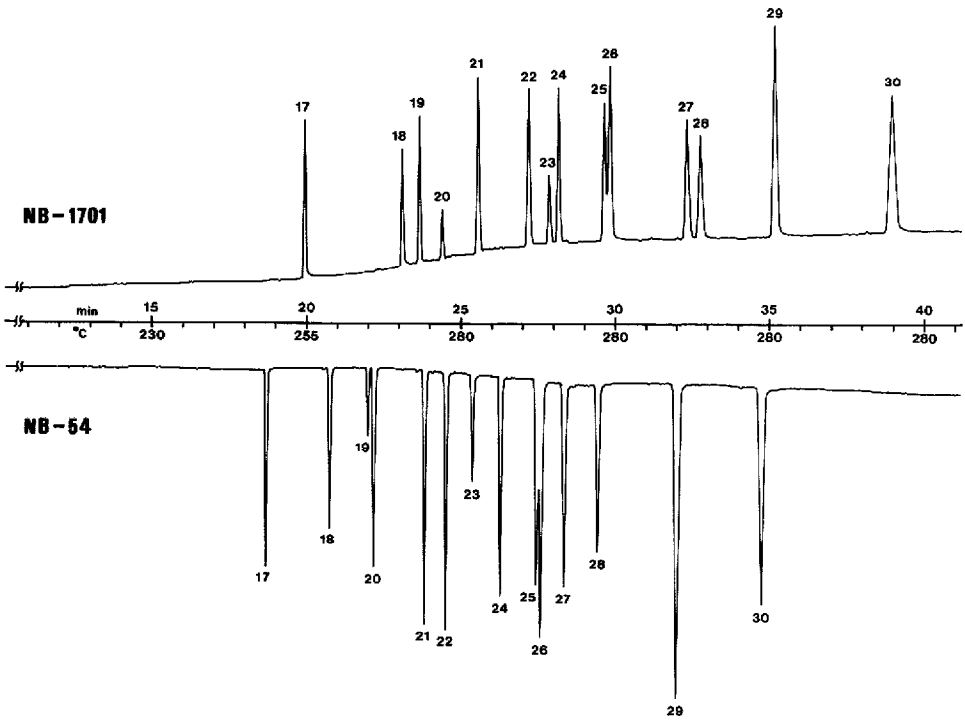
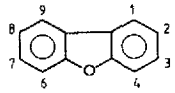


Fig. 2. Chromatogram of a mixture of polychlorinated dibenzofurans (PCDFs), separated on NB-54 and NB-1701 capillary columns under conditions as in Fig. 1. Peaks 17–30 are identified in Table III.

TABLE III

RETENTION DATA FOR POLYCHLORINATED DIBENZOFURANS OBTAINED ON NB-54 AND NB-1701 CAPILLARY COLUMNS

Conditions as in Fig. 2.



Peak No.	*Systematic No.*[a]	*Compound*[b]	*Column*						
			NB-54			*NB-1701*			
			ART[c]	*RRT*[d]	*RRT*[e]	*ART*[c]	*RRT*[d]	*RRT*[e]	*RRT*[f]
17	69	1,3,6,8	18.77	0.902	0.963	19.86	0.863	1.058	0.963
18	83	2,3,7,8	20.81	1.000	0.981	23.01	1.000	1.106	1.017
19	63	1,2,8,9	22.01	1.058	1.003	23.59	1.025	1.072	0.978
20	106	1,3,4,6,8	22.23	1.068	–	24.34	1.058	1.095	–
21	94	1,2,3,7,8	23.90	1.148	0.964	25.47	1.107	1.066	0.965
22	114	2,3,4,7,8	24.59	1.181	–	27.11	1.178	1.102	–
23	96	1,2,3,8,9	25.40	1.220	1.007	27.79	1.208	1.094	1.015
24	116	1,2,3,4,6,8	26.37	1.267	–	28.10	1.221	1.066	–
25	118	1,2,3,4,7,8	27.52	1.322	0.966	29.57	1.285	1.074	0.961
26	121	1,2,3,6,7,8	27.69	1.331	0.968	29.76	1.293	1.075	0.962
27	130	2,3,4,6,7,8	28.41	1.365	–	32.22	1.400	1.134	–
28	120	1,2,3,4,8,9	29.50	1.418	–	32.69	1.421	1.108	–
29	131	1,2,3,4,6,7,8	32.08	1.542	0.943	35.09	1.525	1.094	0.926
30	134	1,2,3,4,7,8,9	34.81	1.673	–	38.86	1.689	1.116	–

[a] Taken from ref. 60.
[b] Numbers indicate the chlorinated positions.
[c] Absolute retention times (min) were measured from sample injection (Fig. 2).
[d] Relative retention time for 18 taken as 1.000.
[e] Relative retention time for the corresponding PCDD isomer taken as 1.000 (Table II).
[f] Relative retention time for the corresponding isomer on NB-54 taken as 1.000.

phases, only compounds 25 and 26 partially overlapping. It should be noted that the predicted retention indices for these two isomers are close together[17], the components being nearly coincident also on polar stationary phases such as Silar 10C[25,44,47] and SP-2330[6]. Owing to the relatively small difference between the polarities of NB-54 and NB-1701 (McReynolds constants *ca.* 320 and 780, respectively), the retention order of the isomers is unaltered. However, if analysed on a polar column, the alterations would be evident based on earlier observations with tetrachlorodibenzofurans on DB-5 (low-polarity) and SP-2330 (polar) stationary phases[15]. This different behaviour of PCDFs is due to their unsymmetrical molecular structure compared with symmetrical PCDDs, shown also by comparison of the retention behaviours of the same PCDD and PCDF isomers (Table III).

CONCLUSIONS

The results show that the mixture of all 30 compounds investigated can be separated on NB-1701, but on NB-54 two additional overlappings are evident, *viz.*, 3 with 9 and 10 with 27. The lower thermal stability of NB-1701 limits the final oven temperature to its maximum of 280°C on NB-54, owing to the double-column system used, resulting in relatively higher retention times for the octachloro isomer (16) particularly on OV-1701 (Fig. 1). However, the use of a column as polar as possible is recommended to achieve the maximum separation, but with highly polar columns the elution order of certain isomers shifts significantly[17], even to the extent that components are not eluted in order of their degrees of chlorination. The latter fact is shown particularly with some PCDF isomers on Silar 10C[25], and also with our preliminary results on a highly polar NB-9C capillary column[61].

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REFERENCES

1 J. W. A. Lustenhouwer, K. Olie and O. Hutzinger, *Chemosphere*, 9 (1980) 501; and references cited therein.
2 W. B. Crummett, *Chemosphere*, 12 (1983) 429; and references cited therein.
3 W. B. Crummett and D. I. Townsend, *Chemosphere*, 13 (1984) 777; and references cited therein.
4 O. Hutzinger, M. J. Blumich, M. van den Berg and K. Olie, *Chemosphere*, 14 (1985) 581; and references cited therein.
5 M. J. Boddington, P. Barrette, D. Grant, R. J. Norstrom, J. J. Ryan and L. Whitby (Guest Editors), *Proceedings of the 4th International Symposium on Chlorinated Dioxins and Related Compounds, Ottawa, October 16–18, 1984; Chemosphere*, 14 (1985) 575–989.
6 C. Rappe, L.-O. Kjeller, P. Bruckmann and K.-H. Hackhe, *Chemosphere*, 17 (1988) 3; and references cited therein.
7 O. Hutzinger, W. Crummett, F. W. Karasek, E. Merian, G. Reggiani, M. Reissinger and S. Safe (Guest Editors), *Proceedings of the 5th International Symposium on Chlorinated Dioxins and Related Compounds, Bayreuth, September 16–19, 1985; Chemosphere*, 15 (1986) 1085–2132.
8 Y. Masuda, O. Hutzinger, F. W. Karasek, J. Nagayama, C. Rappe, S. Safe and H. Yoshimura (Guest Editors), *Proceedings of the 6th International Symposium on Chlorinated Dioxins and Related Compounds, Fukuoka, September 16–19, 1986; Chemosphere*, 16 (1987) 1603–2210.
9 G. A. Eiceman, R. E. Clement and F. W. Karasek, *Anal. Chem.*, 51 (1979) 2343.
10 P. W. Albro, W. B. Crummett, A. E. Dupuy, Jr., M. L. Gross, M. Hanson, R. L. Harless, F. D. Hileman, D. Hilker, C. Jason, J. L. Johnson, L. L. Lamparski, B. P.-Y. Lau, D. D. McDaniel, J. L. Meehan, T. J. Nestrick, M. Nygren, P. O'Keefe, T. L. Peters, C. Rappe, J. J. Ryan, L. M. Smith, D. L. Stalling, N. C. A. Weerasinghe and J. M. Wendling, *Anal. Chem.*, 57 (1985) 2717.
11 F. I. Onuska, R. J. Wilkinson and K. Terry, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 9.
12 J. J. Ryan, R. Lizotte and W. H. Newsome, *J. Chromatogr.*, 303 (1984) 351.
13 F. D. Hileman, M. D. Hale, T. Mazer and R. W. Noble, *Chemosphere*, 14 (1985) 601.
14 M. D. Hale, F. D. Hileman, T. Mazer, T. L. Shell, R. W. Noble and J. J. Brooks, *Anal. Chem.*, 57 (1985) 640; and references cited therein.
15 W. J. Dunn III, M. Koehler, D. L. Stalling and T. R. Schwartz, *Anal. Chem.*, 58 (1986) 1835; and references cited therein.
16 D. S. Waddell, R. K. Boyd, H. S. McKinnon, L. Safe, S. Safe and B. G. Chittim, *Chemosphere*, 16 (1987) 1655; and references cited therein.

17 J. R. Donnely, W. D. Munslow, R. K. Mitchum and G. W. Sovocool, *J. Chromatogr.*, 392 (1987) 51; and references cited therein.
18 H. Y. Tong, D. L. Shore, F. W. Karasek, P. Helland and E. Jellum, *J. Chromatogr.*, 285 (1984) 423.
19 G. Lindström and C. Rappe, *Chemosphere*, 17 (1988) 921.
20 E. R. Barnhart, D. G. Patterson, Jr., N. Tanaka and M. Araki, *J. Chromatogr.*, 445 (1988) 145.
21 H. Beck, K. Eckart, W. Mathar and R. Wittkowski, *Chemosphere*, 17 (1988) 51.
22 G. Eklund, J. R. Pedersen and B. Strömberg, *Chemosphere*, 17 (1988) 575.
23 K. Ballschmiter, I. Braunmiller, R. Niemczyk and M. Swerev, *Chemosphere*, 17 (1988) 995.
24 M. Oehme, P. Fürst, Chr. Krüger, H. A. Meemken and W. Groebel, *Chemosphere*, 17 (1988) 1291.
25 W. V. Ligon, Jr. and R. J. May, *J. Chromatogr.*, 294 (1984) 87.
26 M. Swerev and K. Ballschmiter, *Anal. Chem.*, 59 (1987) 2536.
27 C. E. Parker, P. W. Albro, M.-J. Bobenrieth, T. W. Cochran and J. D. Robinson, *J. Chromatogr.*, 278 (1983) 1.
28 K. Scheidl, F. Wurst and R.-P. Kuna, *Chemosphere*, 15 (1986) 2089.
29 K. Norén, *Chemosphere*, 17 (1988) 39.
30 M. Morita, A. Yasuhara and H. Ito, *Chemosphere*, 16 (1987) 1959.
31 J. Lawrence, F. Onuska, R. Wilkinson and B. K. Afghan, *Chemosphere*, 15 (1986) 1085.
32 M. Oehme and P. Kirschmer, *Anal. Chem.*, 56 (1984) 2754.
33 T. Humppi and K. Heinola, *J. Chromatogr.*, 331 (1985) 410.
34 H.-R. Buser, *Anal. Chem.*, 49 (1977) 918.
35 P. Schmid and M. D. Müller, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 548.
36 M. Swerev and K. Ballschmiter, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 544.
37 U. Riehle, J. Ehmann, M. Swerev and K. Ballschmiter, *Fresenius Z. Anal. Chem.*, 331 (1988) 821.
38 J. Paasivirta, J. Tarhanen, B. Juvonen and P. Vuorinen, *Chemosphere*, 16 (1987) 1787.
39 H.-R. Buser, *Chemosphere*, 16 (1987) 713.
40 H. Thoma, O. Hutzinger, M. Höhn and U. Rapp, *Chemosphere*, 15 (1986) 2115.
41 H.-R. Buser, *Chemosphere*, 17 (1988) 889.
42 S. Herve, P. Heinonen, R. Paukku, M. Knuutila, J. Koistinen and J. Paasivirta, *Chemosphere*, 17 (1988) 1945.
43 A. Munder, H. Buchert, R. Niemczyk, M. Swerev and K. Ballschmiter, *Fresenius Z. Anal. Chem.*, 328 (1987) 639.
44 C. Rappe, M. Nygren, G. Lindström, H.-R. Buser, O. Blaser and C. Wüthrich, *Environ. Sci. Technol.*, 21 (1987) 964.
45 H. Hagenmaier, M. Kraft, H. Brunner and R. Haag, *Environ. Sci. Technol.*, 21 (1987) 1080.
46 H. Hagenmaier, H. Brunner, R. Haag and M. Kraft, *Environ. Sci. Technol.*, 21 (1987) 1085.
47 H. Hagenmaier and H. Brunner, *Chemosphere*, 16 (1987) 1759.
48 W. A. Korfmacher, R. K. Mitchum, F. D. Hileman and T. Mazer, *Chemosphere*, 12 (1983) 1243.
49 S. Marklund, C. Rappe, M. Tysklind and K.-E. Egebäck, *Chemosphere*, 16 (1987) 29.
50 C. Rappe and L.-O. Kjeller, *Chemosphere*, 16 (1987) 1775.
51 S. E. Swanson, C. Rappe, J. Malmström and K. P. Kringstad, *Chemosphere*, 17 (1988) 681.
52 M. Oehme, S. Manø, A. Mikalsen and P. Kirschmer, *Chemosphere*, 15 (1986) 607.
53 M. Oehme, S. Manø and A. Mikalsen, *Chemosphere*, 16 (1987) 143.
54 A. Yasuhara, H. Ito and M. Morita, *Environ. Sci. Technol.*, 21 (1987) 971.
55 O. M. van Berkel, K. Olie and M. van den Berg, *Int. J. Environ. Anal. Chem.*, 34 (1988) 51.
56 T. Wakimoto, N. Kannan, M. Ono, R. Tatsukawa and Y. Masuda, *Chemosphere*, 17 (1988) 743.
57 H. Hagenmaier, M. Kraft, W. Jäger, U. Mayer, K. Lützke and D. Siegel, *Chemosphere*, 15 (1986) 1187.
58 E. S. Lahaniatis, E. Clausen, D. Bieniek and F. Korte, *Chemosphere*, 14 (1985) 233.
59 J. Paasivirta, *Harmful Compounds in the Environment*, Department of Chemistry, University of Jyväskylä, 1988, pp. 1–34.
60 K. Ballschmiter, H. Buchert, R. Niemzyk, A. Munder and M. Swerev, *Chemosphere*, 15 (1986) 901.
61 I. O. O. Korhonen and K. M. Mäntykoski, Unpublished results.