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Gas chromatographic separations of all 136 tetra- to octa-polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans on nine different stationary phases[a]

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ABSTRACT

All 49 polychlorinated dibenzo-*p*-dioxins and 87 polychlorinated dibenzofurans containing 4 to 8 chlorines have been synthesized and purified as individual compounds in quantitative amounts. These standards have been chromatographed on a series of nine fused-silica capillary gas chromatography (GC) columns containing silicone stationary phases of diverse polarity (100% methyl, 5% phenyl methyl, 50% phenyl methyl, 50% methyl trifluoropropyl, 50%, 75%, 90% and 100% cyanopropyl and liquid crystalline smectic). The data, expressed in a series of GC chromatograms and in tables of relative retention times, are the most comprehensive to date with regard to individual congeners and variety of stationary phases and provide a confirmation of much earlier work. The information shows that all 136 compounds, including the biologically important 2,3,7,8-substituted congeners, can be separated from each other mostly with two stationary phases. However, possible variation in GC conditions and stationary phases necessitates assessment of the resolution of near eluting isomers. Comparisons and contrasts to previously published reports have also been noted.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two classes of environmental contaminants which are present as impurities in a variety of industrial chemicals such as chlorophenols and polychlorinated biphenyls (PCBs). They are also formed in heat processes particularly in the incineration of municipal waste [1], and recently have been found in the bleaching of pulp and paper [2,3]. The PCDDs (49 congeners) and PCDFs (87 congeners) of

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TABLE I

NUMBER OF ISOMERS AND CONGENERS OF THE PCDDs AND PCDFs

Chlorine number homologue	Acronyms[a]	Number of isomers		Total
		PCDD	PCDF	
1	MCDD/MCDF	2	4	6
2	DiCDD/DiCDF	10	16	26
3	TrCDD/TrCDF	14	28	42
4	TCDD/TCDF	22	38	60
5	PnCDD/PnCDF	14	28	42
6	HxCDD/HxCDF	10	16	26
7	HpCDD/HpCDF	2	4	6
8	OCDD/OCDF	1	1	2
Total		Number of congeners		
1–8		75	135	210
1–3		26	48	74
4–6		46	82	128
4–8		49	87	136

[a] CDD = chlorinated dibenzo-*p*-dioxin; CDF = chlorinated dibenzofuran; M = mono; Di = di; Tr = tri; T = tetra; Pn = penta; Hx = hexa; Hp = hepta; O = octa.

biological interest contain 4 to 8 chlorines and these along with their acronyms are shown in detail in Table I. For brevity and simplicity when describing and comparing different congeners, the chlorine substitution is usually designated without using commas to separate the arabic numbers. PCDDs and PCDFs with the 2,3,7,8-configuration (17 congeners) are the most toxic in experimental animals. These congeners have been found in wildlife [4], human tissues [5], and food samples [6], and are the most important for purposes of identification and quantification. Mass spectrometry (MS) provides unequivocal identification of the elemental composition (molecular formula) of a substance, but gas chromatographic (GC) techniques are required to separate and identify those compounds having the same elemental composition but different structure or constitution (isomers). For example, MS can detect all 22 TCDD isomers but GC is needed to specify which of these has the 2,3,7,8-substitution.

A plethora of data has been published [7–44] in the last 10 years on the separation of the isomers and congeners of PCDDs/PCDFs using gas chromatography. In the late 1970s and early 1980s most of this work was performed using stationary phases coated on inert supports (packed GC columns). In the last 5 years or so virtually all separations have been carried out on the better resolving capillary columns where the stationary phase is coated on or chemically bonded to the glass surface of the wall. In particular, studies on the separation of all 38 TCDFs and 22 TCDDs on both non-polar (methyl silicone) [15,16,35] and polar (cyanopropyl silicone) [14–16, 18,23,35,40] columns are available and the GC properties of all 128 PCDDs/PCDFs containing 4 to 6 chlorines are known for both non-polar and polar phases [9,11,13,19–22, 25–29,30, 32–34,39,42]. However, information on GC separa-

tions is often lacking or incomplete for: (a) the homologues higher than tetrachloro for medium polar (methyl–phenyl silicones) phases and (b) for all homologues on certain uncommon phases (*e.g.* methyl–trifluoropropyl silicones and liquid crystalline). In addition much of the data are scattered throughout the literature, and are incomplete for the congeners of biological interest. Some discrepancies also exist between separations and relative peak assignments reported by various research groups. As a result, we obtained authentic standards of all 136 PCDDs/PCDFs of biological interest in pure separate quantitative amounts (not mixtures) by synthesis and exchange. Their elution order and separations were then examined on a wide variety of stationary phases on either bonded or wall-coated fused-silica capillary columns using the liquid phases most commonly in the field as well as these advocated by Yancey [45–47] in his review of liquid phases. However, this report does not attempt to predict or provide a theoretical model for separation based on molecular structure.

EXPERIMENTAL

Definition and nomenclature

The terms, congener, isomer, and homologue are often used to describe the different kinds of PCDDs and PCDFs but unfortunately the usage of these terms has been inconsistent and confusing. In this paper we use congener to refer to any member of the class of PCDDs or PCDFs regardless of the degree of chlorination. In this respect there are 75 possible congeners of PCDDs and 135 congeners of the PCDFs (Table I). Isomers are compounds with the same elemental compositon or molecular formula (number and kinds of atoms) but with different structural or configurational arrangement. It is well known that there are 22 structural isomers of the TCDDs. Homologues usually refer to groups of compounds with a common structure (*e.g.* CDD or CDF) but differing by a constant increment of common atoms (*e.g.* number of chlorines). Mass spectrometry (MS) can readily distinguish one homologue group of PCDDs/PCDFs from another simply by their mass to charge ratio. However, MS is generally unable to specify which isomer of any homologue is present. Such an assignment requires the technique of gas chromatography. A combination of both GC and MS techniques permits, in theory, the identification of all congeners of the PCDDs/PCDFs.

The nomenclature for the numbering of the chlorine positions in the CDD and CDF ring system is that given in Fig. 1 subscribing to the usage of Chemical Abstracts

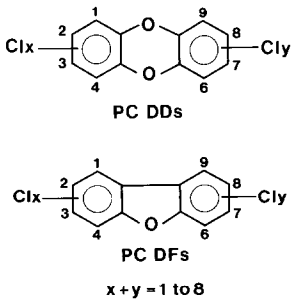

Fig. 1. Chemical structures of the congeners of PCDDs/PCDFs.

TABLE II

SOURCES AND PURITY OF THE 49 PCDDs WITH 4 TO 8 CHLORINES

No.	Isomer	CA registry number	Systematic number	Base hex number	Source and purity[a]
TCDDs					
1	1234	30746-58-8	162	f0D	Analabs, U.S.A.; 98%
2	1236	71669-25-5	163	78D	D. Firestone, U.S.A.; S1 with 1239-D (3:2 mixture); RP-HPLC, 97%
3	1237	67028-18-6	164	74D	(a) KOR Isotope, U.S.A.; S1, mixture with 1238-D (b) Pyrolysis (3); RP-HPLC (3), 98% (c) Photolysis of 12367-D
4	1238	53555-02-5	165	72D	(a) KOR Isotope; S1, mixture with 1237-D (b) Pyrolysis (3); RP-HPLC (3), 97% (c) Photolysis of 12389-D
5	1239	71669-26-6	166	71D	D. Firestone; S1, mixture with 1236-D (2:3); RP-HPLC (2), 97%
6	1246	71669-27-7	167	b8D	Pyrolysis; RP-HPLC, 97%
7	1247	71669-28-8	168	b4D	Pyrolysis (2); RP-HPLC; NP-HPLC (2), 95%
8	1248	71669-29-9	169	b2D	Pyrolysis (2); RP-HPLC; NP-HPLC (2), 90%
9	1249	71665-99-1	170	b1D	Pyrolysis; RP-HPLC (2), 97%
10	1267	40581-90-6	171	3CD	Pyrolysis (2); RP-HPLC, 95%
11	1268	67323-56-2	172	3aD	Pyrolysis (2); RP-HPLC (3), 95%
12	1269	40581-91-7	173	39D	Pyrolysis; RP-HPLC, 95%
13	1278	34816-53-0	174	36D	(a) KOR Isotope; S1, 98% (b) Pyrolysis; RP-HPLC, 97%
14	1279	71669-23-3	175	35D	Pyrolysis (2); RP-HPLC (3), 95%
15	1289	62470-54-6	176	33D	Pyrolysis (2); RP-HPLC (2), 95%
16	1368	33423-92-6	177	5aD	(a) Ultra Scientific, U.S.A.; 98% (b) Pyrolysis (2); RP-HPLC, 97% (c) D. Firestone; 3:1 mixture with 1379-D
17	1369	71669-24-4	178	59D	Pyrolysis; RP-HPLC (2), 95%
18	1378	50586-46-1	179	56D	KOR Isotope; S1; 98%
19	1379	62470-53-5	180	55D	(a) Pyrolysis; RP-HPLC, 95% (b) D. Firestone; 1:3 mixture with 1368-D
20	1469	40581-93-9	181	99D	Pyrolysis; RP-HPLC, 95%
21	1478	40581-94-0	182	96D	Pyrolysis; RP-HPLC (2), 95%
22	2378	1746-01-6	183	66D	(a) Dow Chemical, U.S.A.; 95% (b) P. Kearney, U.S.A.; 95% (c) D. Firestone; 98% (d) National Bureau Standards, Washington, U.S.A., 98%
PnCDDs					
1	12346	67028-19-7	184	f8D	Pyrolysis (2); RP-HPLC, 98%
2	12347	39227-61-7	185	f4D	W. Miles, Canada; S1; 97%
3	12367	71925-15-0	186	7CD	Pyrolysis (2); RP-HPLC (3); 81% pure; 12467-D, 8%; 12489-D, 11%
4	12368	71925-16-1	187	7aD	Pyrolysis; RP-HPLC, 90%, some 12479-D
5	12369	82291-34-7	188	79D	Pyrolysis; RP-HPLC (3), 90%, some 12479-D
6	12378	40321-76-4	189	76D	(a) Pyrolysis (2); RP-HPLC (b) W. Miles; S1; 97% (c) D. Firestone; S1; 97%,

TABLE II *(continued)*

No.	Isomer	CA registry number	Systematic number	Base hex number	Source and purity[a]
7	12379	71925-17-2	190	75D	Pyrolysis; RP-HPLC, 98%
8	12389	71925-18-3	191	73D	Pyrolysis (2); RP-HPLC, 98%
9	12467	82291-35-8	192	bcD	Pyrolysis (2); RP-HPLC (2), 97%
10	12468	71998-76-0	193	baD	Pyrolysis (3); RP-HPLC (3), 90% pure, rest 12479-D
11	12469	82291-36-9	194	b9D	Pyrolysis (2); RP-HPLC (2) 98%
12	12478	58802-08-7	195	b6D	D. Firestone; S1; 98%
13	12479	82291-37-0	196	b5D	Pyrolysis (3); RP-HPLC (3), 90%, rest 12468-D
14	12489	82291-38-1	197	b3D	Pyrolysis (2); RP-HPLC (3), 96%
HxCDDs					
1	123467	58200-66-1	198	fcD	Pyrolysis (2); RP-HPLC (3), 97%
2	123468	58200-67-2	199	faD	Pyrolysis (2); RP-HPLC, 97%
3	123469	58200-68-3	200	f9D	Pyrolysis (90%); RP-HPLC (4), contains 10% 124679/124689-D
4	123478	39227-28-6	201	f6D	KOR Isotopes; S1; 98%
5	123678	57653-85-7	202	7eD	(a) Pyrolysis (b) J. Moore, U.S.A.; S2; 98%
6	123679	64461-98-9	203	7dD	(a) D. Firestone; S1, 1:1 mixture with 123689-D, m.p. 202–205°C; RP-HPLC (2), 96%, rest 123689-D (b) J. Moore; S1, 1:1 mixture with 123689-D (c) Pyrolysis (2), mixtures with 123689-D; RP-HPLC (2)
7	123689	58200-69-4	204	7bD	(a) D. Firestone; S1, 80% mixture with 123679-D, m.p. 233–242°C; RP-HPLC (2), 95% pure, rest 123679-D (b) J. Moore; S1, 1:1 mixture with 123679-D (c) Pyrolysis (2), mixtures with 123679-D; RP-HPLC (2)
8	123789	19408-74-3	205	77D	(a) Pyrolysis mixture (b) D. Firestone; S2, 98%
9	124679	39227-62-8	206	bdD	(a) Pyrolysis (2); RP-HPLC (3), 80% pure, 3% 123679-D, 17% 124689-D (b) A. Dobbs, U.K.; 1:2 mixture with 124689-D (c) D. Firestone; pyrolysis mixture
10	124689	58802-09-8	207	bbD	(a) Pyrolysis (2); RP-HPLC (3), 96% pure (b) A. Dobbs; 2:1 mixture with 124679-D (c) D. Firestone; pyrolysis mixture
HpCDD					
1	1234678	35822-46-9	208	feD	(a) KOR Isotope; S1; 98% (b) Pyrolysis
2	1234679	58200-70-7	209	fdD	(a) D. Firestone; S1; 98% (b) Pyrolysis (c) A. Dobbs; 98%
OCDD					
1	12346789	3268-87-9	210	ffD	(a) Analabs; 99% (b) Pyrolysis

[a] Pyrolysis: chlorophenol(s) in equal molar amounts with copper filings and potassium carbonate dissolved in freshly prepared excess methanolic KOH, evaporated to dryness, and heated at 280–300°C for 1 h as in refs. 11 and 17; number in parenthesis after pyrolysis refers to different reaction mixtures of chlorophenols or routes used to obtain the same product. S1: synthesis by alkali condensation of chlorocatechol or chloroguiacol with chloronitrobenzene. S2: synthesis by alkali condensation of 2-bromo-3,4,5-trichlorophenol followed by selective crystallization of mixture. RP-HPLC: reversed-phase high-performance liquid chromatography (number in parenthesis refers to number of cycles needed to obtain stated purity). NP-HPLC: normal-phase HPLC.

(CA). In addition, CA nomenclature states that the lowest number possible must be used when alternatives exist. In particular, in the TCDF series (*cf.* Table I for acronyms), 1678 is used and not 2349; in the PnCDF series, 12678, 12679, 13678, and 14678 are the correct numbering and not the alternatives 23489, 13489, 23479 and 23469, respectively, and; in the HxCDF series, the isomeric designations are 124679 and 134678 and not 134689 and 234679, respectively. All of the above alternatives have been used in some instances in the literature.

Standards

PCDDs. All 49 congeners of the PCDDs of homologue from tetrachloro- to octachloro- were obtained as authentic individual standards in low milligram amounts either by synthesis [pyrolysis of 10–25 mg quantities of the appropriate chlorophenols or by two other routes (S1 and S2) as noted in Table II and refs. 11 and 17], or by exchange with or donation from other research groups. Table II gives the CA registry number, the systematic number [28] and the hex base number [48] along with the source, method of synthesis, and purity for each congener. The pyrolysis reaction products and other mixtures were purified to single compounds by repeated separation on preparative scale reversed-phase (RP) high-performance liquid chromatography (HPLC) columns containing octyldecylsilane (ODS) as stationary phase. The eluents were various combinations of methanol, ethanol, isopropanol and acetonitrile, some with the addition of small amounts (1 to 10%) of water similar to previous reports [10,14,15,22,23]. Several passes by HPLC were needed in some cases in order to obtain the purity stated in Table II. Particularly difficult congeners to separate and purify were the combinations of 1247/1248, 12468/12479, 124679/124689 and 123679/123689 and the congeners 12367, 12368 and 123469 all of which contained small amounts (3 to 10%) of other congeners. The isomer pair 1247/1248 was the only PCDD which could not be resolved by RP-HPLC but did separate nicely on normal-phase HPLC.

The assignment of the configuration of each PCDD was unequivocal in most cases. Some PCDDs/PCDFs have been authenticated by X-ray diffraction [49,50] and these primary standards have been compared in the literature to other congeners with regard to their physical and chemical properties. For instance, it has been established [11,17] by photolysis of congeners of known constitution that those congeners containing adjacent chlorines on both sides of the planar ring next to the oxygen (*e.g.* 123789-HxCDD, 12389-PnCDD and 1289-TCDD) are sterically strained and are the isomers that elute last on most GC columns. Because of the Smiles rearrangement [51,52], pyrolysis of many chlorinated phenols generated two isomers which differed only in the relative orientation of the two lateral aromatic rings. By judicious choice of the starting material, other mixtures can be synthesized containing one of a pair from a previous pyrolysis. This allowed an assignment to be made in most cases as detailed earlier [17]. In addition, in many cases certain standards were available from other research groups or commercial sources. These were sometimes synthesized by other routes (*e.g.* condensation of a chlorocatechol with a nitrobenzene) and could be directly compared to one synthesized by the chlorophenol route. In one case of Smiles-rearranged products, the 1237/1238-TCDD pair, specific assignment could be made. Photolysis of individual aliquots of 12367 and 12389-PnCDD caused loss of chlorine giving TCDD mixtures. Comparison of these TCDD mixtures on GC to the two isomers comprising the 1237/1238-TCDD pair from the Smiles rearrangement

(themselves separable by RP-HPLC) showed that 1237-TCDD eluted first on polar GC columns but second on RP-HPLC. Conversely, the peak from the 1237/1238-TCDD pair eluting second on polar GC columns but first on RP-HPLC was in fact the 1238-TCDD isomer. Six congener pairs synthesized as mixtures, 1246/1249-TCDD, 1247/1248-TCDD, 12468/12479-PnCDD, 12467/12489-PnCDD, 124679/124689-HxCDD, and 123679/123689-HxCDD could not be unequivocably assigned. In these cases, the isomer with the lowest numerical nomenclature designation has been assigned as the earliest eluting compound on RP-HPLC (NP-HPLC for the 1247/1248-TCDD pair). For example with the pair 1246/1249-TCDD, the first eluting isomer on RP-HPLC has been assigned arbitrarily as 1246-TCDD and this designation is used in the GC chromatograms. All standards were checked for purity using GC with electron capture (EC) detection supplemented in some cases with flame detection. Identity was confirmed by using GC with MS detection.

Purified amounts (50 to 500 μg) of standards were weighed on a Cahn 26 electrobalance which has been calibrated for accuracy against a known mass. Precision of weighing of 200 μg quantities was less than 2%. Usually a stock solution of the weighed material was made up in 10 ml of toluene in a volumetric flask and serial dilutions of this concentration were caried out to produce 1.0 ng/μl and 0.1 ng/μl solutions in 5 ml volumes.

PCDFs. Most of the 87 PCDFs of homologue tetrachloro- to octachloro- were synthesized either by dehydrogenation of the corresponding chlorinated diphenyl ether [53] (synthesized from the chlorinated phenol and chlorinated diphenyl iodonium salt; route S2 in Table III) or by condensation of the corresponding chlorophenol and chloronitrobenzene followed by reductive cyclization [20] (route S1 in Table III). In the few cases where a PCDF could not be synthesized from these two routes, they were prepared by two other methods (S3 or S4 in Table III) or obtained from other research groups or commercial sources. The reaction mixtures were separated by RP-HPLC in a similar fashion as for the PCDDs except that fewer passes were needed to obtain the stated purity since PCDF mixtures show greater resolution on RP-HPLC than do the PCDDs. Impurities in the PCDFs mixtures were often one homologue lower than the desired product *i.e.* dechlorination rather than dehydrochlorination. Assignment of isomeric structure of the PCDFs is given in more detail in refs. 15, 16 and 22 with the additional support in this work that many of the PCDFs were supported by NMR data [20].

Instrumentation

The gas chromatographs used were Varian models 3500 and 6000 equipped with capillary columns and on-column injectors. The ovens and injectors could be programmed independently of each other. The method of injection was by the solute focusing on-column technique whereby the injector was kept at 80°C [below the boiling point of the solvent (usually toluene)], and then the injector heat ramped quickly (1 to 3 min) to 230–260°C – the final column temperature. The oven and the column itself were initially held at 120°C, just above the boiling temperature of the solvent, then heated rapidly to 160–180°C and then slowly (2 to 3°C per min) to the final temperature. Carrier gas for the capillary columns was helium at a linear velocity of 30 cm/s corresponding to a volume flow of about 2.0 ml/min. Chart speed for the chromatograms varied between 2.0 and 4.0 cm/s and volume of injection between 0.6

TABLE III

SOURCES AND PURITY OF THE 87 PCDFs WITH 4 TO 8 CHLORINES

No.	Isomer	CA registry number	Systematic number	Base hex number	Source and purity[a]
TCDFs					
1	1234	24478-72-6	49	f0F	H. Markens, The Netherlands; 98%
2	1236	83704-21-6	50	78F	S1; 97%
3	1237	83704-22-7	51	74F	S1; 97%
4	1238	62615-08-1	52	72F	S1; 97%
5	1239	83704-23-8	53	71F	(a) Wellington, Ontario, Canada; 98% (b) C. Rappe, Sweden; S3 with 1237-F; 98%
6	1246	71998-73-7	54	b8F	S1; 95%
7	1247	83719-40-8	55	b4F	S1; 98%
8	1248	64126-87-0	56	b2F	(a) S2; 97% (b) D. Firestone, U.S.A.
9	1249	83704-24-9	57	b1F	S1; 98%
10	1267	83704-25-0	58	3CF	S1; 97%
11	1268	83710-07-0	59	3aF	S2 with 2368-F; RP-HPLC, 97%
12	1269	70648-18-9	60	39F	(a) C. Rappe; S2 with 1469-F, 98% (b) Wellington; mixture with 1469-F
13	1278	58802-20-3	61	3bF	(a) S1; 98% (b) S2; with 2378-F; RP-HPLC, 98% (c) D. Firestone
14	1279	83704-26-1	62	35F	S1; 98%
15	1289	70648-22-5	63	33F	(a) S2; mixture with 2378-F, 1278-F, <1% yield; RP-HPLC (3) (b) C. Rappe; S2; 95%
16	1346	83704-27-2	64	d8F	S1; 95%
17	1347	70648-16-7	65	d4F	S1; 97%
18	1348	92341-04-3	66	d2F	S1; 98%
19	1349	83704-28-3	67	d1F	(a) Wellington; 95% (b) C. Rappe; S3; with 1347-F, 95%
20	1367	57117-36-9	68	5cF	(a) S1; 98% (b) Canadian Wildlife, Ottawa, Canada; qual., 95%
21	1368	71998-72-6	69	5aF	S1; 98%
22	1369	83690-98-6	70	59F	S1; 98%
23	1378	57117-35-8	71	56F	(a) S1; 98% (b) Canadian Wildlife; qual., 95%
24	1379	64560-17-4	72	55F	S1; 98%
25	1467	66794-59-0	73	9cF	S1; 98%
26	1468	82911-58-8	74	9aF	D. Firestone; 98%
27	1469	70648-19-0	75	99F	(a) C. Rappe; S2; 95% (b) Wellington: 80% with 1269-F
28	1478	83704-29-4	76	96F	S1; 98%
29	1678	83704-33-0	77	1dF	S1; 93%
30	2346	83704-30-7	78	d8F	S1; 98%
31	2347	83704-31-8	79	d4F	S1; 98%
32	2348	83704-32-9	80	d2F	S1; 98%
33	2367	57117-39-2	81	6cF	(a) S1; 98% (b) Canadian Wildlife; qual., 95%
34	2368	57117-37-0	82	6aF	(a) S2 with 1268-F; 98%; RP-HPLC (b) J. McKinney, U.S.A.; 98%

TABLE III *(continued)*

No.	Isomer	CA registry number	Systematic number	Base hex number	Source and purity[a]
35	2378	51207-31-9	83	66F	(a) J. McKinney; 94% (b) KOR Isotope, U.S.A.; 98% (c) D. Firestone; 95%
36	2467	57117-38-1	84	acF	(a) S1; 98% (b) Canadian Wildlife; qual., 95%
37	2468	58802-19-0	85	aaF	(a) S1; 98% (b) D. Firestone; 98%
38	3467	57117-40-5	86	ccF	(a) S1; 98% (b) Canadian Wildlife; qual., mixture
PnCDFs					
1	12346	83704-47-6	87	f8F	S1; 97%
2	12347	83704-48-7	88	f4F	S1; 99%
3	12348	67517-48-0	89	f2F	(a) S2; 98% (b) C. Rappe; S2; 98%
4	12349	83704-49-8	90	f1F	S1; 98%
5	12367	57117-42-7	91	7cF	(a) S1; 98% (b) Canadian Wildlife; 98%
6	12368	83704-51-2	92	7aF	(a) S2; 92% (b) C. Rappe; S2; 98%
7	12369	83704-52-3	93	79F	C. Rappe; S2; 98%
8	12378	57117-41-6	94	76F	(a) S2; with 12389-F; RP-HPLC, 98% (b) H. Poiger, Switzerland; qual., 98% (c) Canadian Wildlife; 98%
9	12379	83704-53-4	95	75F	(a) Wellington; 98% (b) C. Rappe; S3; 98%
10	12389	83704-54-5	96	73F	S2 with 12378-F; RP-HPLC, 98%
11	12467	58802-15-6	97	bcF	S1; 97%
12	12468	69698-57-3	98	baF	S2; 96%
13	12469	70648-24-7	99	b9F	S1; 99%
14	12478	58802-15-6	100	b6F	(a) D. Firestone; 98% (b) S2; with 12489-F; RP-HPLC (2), 98%
15	12479	71998-74-8	101	b5F	S1; 98%
16	12489	70648-23-6	102	b3F	S2; with 12478-F; RP-HPLC (2), 98%
17	12678	69433-00-7	103	3eF	S2; with 23478-F; RP-HPLC, 98%
18	12679	70872-82-1	104	3dF	C. Rappe; S2, 98%
19	13467	83704-36-3	105	dcF	S1; 98%
20	13468	83704-55-6	106	daF	(a) S1; 98% (b) C. Rappe; S2; 98%
21	13469	70648-15-6	107	d9F	C. Rappe; S2; 98%
22	13478	58802-16-7	108	d6F	S1; 98%
23	13479	70648-15-6	109	d5F	(a) S1; 98% (b) C. Rappe; S3; 96%
24	13678	70648-21-4	110	5eF	Wellington; 98%
25	14678	83704-35-2	111	9eF	Wellington; 98%
26	23467	57117-43-8	112	ecF	(a) S1; 98% (b) Canadian Wildlife; 97%
27	23468	67481-22-5	113	eaF	S2; 98%
28	23478	57117-31-4	114	e6F	(a) S2; with 12678-F; RP-HPLC, 98% (b) S1; 98% (c) H. Poiger; qual. (d) Canadian Wildlife; 98%

(Continued on p. 140)

TABLE III *(continued)*

No.	Isomer	CA registry number	Systematic number	Base hex number	Source and purity[a]
HxCDFs					
1	123467	79060-60-9	115	fcF	S1; 98%
2	123468	69698-60-8	116	faF	S2; 98%
3	123469	91538-83-9	117	f9F	S1; 98%
4	123478	70648-26-9	118	f6F	(a) S2; with 123489-F; RP-HPLC, 95% (b) Cambridge Isotope, U.S.A.; 98%
5	123479	91538-84-0	119	f5F	S1; 98%
6	123489	92341-07-6	120	f3F	S2 with 123478-F; RP-HPLC (2), 98%
7	123678	57117-44-9	121	7eF	(a) Canadian Wildlife; 98% (b) S2; 98%
8	123679	92341-06-5	122	7dF	C. Rappe; S3; 98%
9	123689	75198-38-8	123	7bF	S2; RP-HPLC; 98%
10	123789	72918-21-9	124	77F	(a) Cambridge Isotope; 98% (b) C. Rappe, S3; 98%
11	124678	67562-40-7	125	bcF	S2; 98%
12	124679	75627-02-0	126	bdF	S2; RP-HPLC, 98%
13	124689	69698-59-5	127	bbF	S2; RP-HPLC, 98%
14	134678	71998-75-9	128	deF	S2; 98%
15	134679	92341-05-4	129	ddF	(a) Wellington; 70% (b) C. Rappe; S3; 98%
16	234678	60851-34-5	130	eeF	(a) S2; 98% (b) Canadian Wildlife; mixture
HpCDFs					
1	1234678	67562-39-4	131	feF	S2; 98%
2	1234679	70648-25-8	132	fdF	S2; RP-HPLC, 98%
3	1234689	69698-58-4	133	fbF	D. Firestone; 98%
4	1234789	55673-89-7	134	f7F	S2; RP-HPLC; 98%
OCDF					
1	12346789	1010-77-1	135	ffF	(1) Analabs, U.S.A.; 98% (2) S2; 98%

[a] S1 Synthesis from corresponding chlorophenol and chloronitrobenzene followed by reductive cyclization [20].

S2 Synthesis from corresponding chlorophenol and chlorodiphenyl iodonium salt to chlorodiphenyl ether followed by palladium acetate cyclization [53].

S3 Synthesis from corresponding chlorophenol and iodobenzene followed by palladium acetate cyclization [53].

S4 Synthesis by nucleophilic displacement of corresponding chlorophenol on chlorobenzene followed by palladium acetate cyclization.

RP-HPLC Reversed phase high-performance liquid chromatography (number in parenthesis is number of collection cycles needed to obtain stated purity).

and 2.0 μl. Detection was usually carried out with a nickel-63 (8 mCi) electron-capture detector kept at 300°C with a nitrogen make-up gas flow of 20 ml/min. A flame ionization detector with air and hydrogen gases was used to monitor impurities in certain cases.

GC capillary columns

Table IV lists, for each GC stationary phase, the manufacturer, coating,

dimensions and temperature programming. These polysiloxane columns are grouped as follows: (i) non-polar (DB-1; 100% methyl and DB-5; 5% phenyl); (ii) medium polar (DB-17, OV-17; 50% phenyl-methyl and DB-210; trifluoropropyl); (iii) polar (DB-225, CPS-1, SP-2331, CP-Sil 88; all cyanopropyl) and (iv) other (SB-smectic).

The chromatograms shown in the figures for the homologues of the PCDDs/PCDFs have been derived from injection of six composite standards of about 0.2 ng/μl each of all isomers of a specific homologue (Table I). Since the analytes have been detected using electron-capture detection (ECD), the absolute response for a given isomer varied by as much as an order of magnitude even though equal amounts were injected. Assignment of a given GC peak to a specific isomer within a group was made by the separate injection of solutions containing one or two isomers along with a retention time (RT) standard, the earliest eluting isomer of that homologue group. These RT reference standards were: (1) for the PCDDs; 1368-TCDD, 12468-PnCDD and 124679-HxCDD and (2) for the PCDFs; 1368-TCDF, 13468-PnCDF and 123468-HxCDF. A combination of results from these injections allowed an unequivocable assignment of the elution order of a specific isomer within a composite mixture. As the retention time windows of most homologue groups of the PCDDs/PCDFs overlap to some extent on capillary columns, particularly polar phases, the injections were carried out by individual homologues. Isomers which co-eluted or eluted near each other were co-injected to define further their degree of resolution.

RESULTS

Three mixtures of the PCDDs (22 tetra, 14 penta and 10 hexa) and three mixtures of the PCDFs (38 tetra, 28 penta and 16 hexa) were prepared at a concentration of 0.2 ng/μl for each congener. The GC elution pattern of these six solutions for nine different GC stationary phases on capillary columns are presented in Figs. 2–10 and their relative retention times (RRT) are listed in Tables V–XIII. The elution order, and degree of separation are best seen from the figures which represent possible separations when all isomers are present in a mixture. For those isomers which did not produce two peaks by co-injection even though they had slightly different relative retention time (RRT), the one first reported on the figure has the shorter RRT. The RRT in the nine tables are based on the earliest eluting isomer of that particular group being arbitrarily assigned a value of 1.000. The RRT of the six RT reference standards are also listed in each table enabling an estimate to be made of the degree of overlap between homologues as a function of stationary phase. The absolute retention time of a selected isomer can be approximated from the tables but should be used only for guidance since this parameter will change from column to column, with usage, and GC conditions. The higher chlorinated hepta- and octa-congeners are not shown in these figures and tables since they are readily resolved from each other on all columns investigated. For all columns, the elution order of the PCDDs is 1234679 and 1234678 for the two hepta isomers followed by octa-dioxin. For the PCDFs, the corresponding elution order for the four hepta isomers is 1234678, 1234679, 1234689 and 1234789, and then octa-furan.

As mentioned in he experimental part, six pairs of PCDDs (12 congeners), separable by HPLC, could only be effectively separated on GC with the liquid crystalline smectic phase. However their exact structure and hence elution order on

TABLE IV

GC SILICONE FUSED-SILICA CAPILLARY COLUMNS USED FOR SEPARATION OF PCDDs AND PCDFs AND THEIR TEMPERATURE PROGRAMS

No.	Name	Manufacturer	Coating and type	Length (m)	Inner diameter (mm)	Film thickness (μm)	Program
1	DB-1	J&W Scientific, CA, U.S.A.	dimethyl (100%), bonded	60	0.32	0.25	120 (1 min) to 180°C (50°C/min) to 280°C (3°C/min)
2	DB-5	J&W Scientific,	methyl (95%) phenyl (5%), bonded	30	0.32	0.25	120 (1 min) to 180°C (50°C/min) to 280°C (3°C/min)
3a	DB-17	J&W Scientific,	methyl (50%) phenyl (50%), bonded	30	0.32	0.25	120 (1 min) to 160°C (20°C/min) to 280°C (3°C/min)
3b	OV-17	Quadrex, New Haven, CT, U.S.A.	methyl (50%) phenyl (50%), bonded	50	0.32	0.25	120 (1 min) to 160°C (20°C/min) to 280°C (3°C/min)
4	DB-210	J&W Scientific,	methyl trifluoropropyl (100%), bonded	30	0.32	0.25	120 (0 min) to 160°C (20°C/min) to 240°C (2°C/min)
5	DB-225	J&W Scientific,	methylcyanopropyl (50%) methyl-phenyl (50%), bonded	30	0.32	0.25	120 (0 min) to 160°C (20°C/min) to 240°C (2°C/min)
6	CPS-1	Quadrex	methylcyanopropyl (75%) phenyl-methyl propyl (25%), bonded	50	0.25	0.25	120 (1 min) to 180°C (30°C/min) to 230°C (2°C/min)
7	SP-2331	Supelco, PA, U.S.A.	biscyanopropyl (90%) phenylcyanopropyl 1:1 (10%), wall coated	60	0.25	0.20	120 (1 min) to 200°C (50°C/min) to 260°C (2°C/min)
8	CP-Sil 88	Chrompack, Middelburg, The Netherlands	biscyanopropyl (100%), wall coated	50	0.22	0.20	150 (0 min) to 180°C (30°C/min) to 230°C (2°C/min)
9	SB-Smectic	Lee Scientific Salt Lake City, UT, U.S.A.	liquid crystalline methyl (80%) diphenyl carboxylic ester (20%), wall coated	25	0.32	0.15	100 (1 min) to 180°C (30°C/min) to 230°C (3°C/min)

GC (either a then b or b then a) could not be definitely assigned. Since these congeners have arbitrarily been assigned with the lowest number in nomenclature eluting first on RP-HPLC, this uncertainly is noted by an asterisk for the data from the smectic column in Fig. 10b and Table XIII. The actual structure of these pairs and hence their GC and HPLC elution order could be determined either by chemical means (dechlorination or chlorination to known congeners) or by physical means (X-ray diffraction crystallography or GC–matrix isolation Fourier-transform infrared spectroscopy).

DISCUSSION

The separations shown in the figures and the RRT in the tables are those that can be obtained using the standards, GC columns, and conditions as described in the experimental section. No particular effort was made to optimize GC conditions such as injector temperature, type of injection, gas flow, temperature programming or other variables to maximize resolution of certain congeners paricularly those which are 2,3,7,8-substituted. Thus it may be possible to obtain slightly different separations than those listed by using other conditions. In this regard we have compared separations on columns purchased at different times from the same manufacturer and with different lot numbers. With both DB-5 and DB-210, identical separations and patterns were obtained from both columns. In the case of the cyanopropyl phases, CP-Sil 88 and SP-2331, columns purchased at different times showed slight differences in resolution in isolated cases *e.g.* isomers co-eluting on one column were found to have some degree of separation on a second different column.

One phenomenon we did notice with the SP-2331 column was the change in elution order and even improved separation as the column deteriorated. After several months of use, the chromatographic peak shape degraded as evidenced by tailing peaks —a phenomenon often attributed to oxygen attack on the stationary phase. Nevertheless, a few separations now occurred which previously with a new column and better peak shape were not possible. For example, 12378-PnCDF was completely separated from the previous co-eluter 12348-PnCDF (now earlier) but co-eluted with the previously separated 12346-PnCDF. 1678-TCDF and 1234-TCDF were now separate peaks on the deteriorated column but co-eluted on the new chromatographic column. On the other hand, 12378-PnCDD and 12369-PnCDD now co-eluted on the degraded column where previously they were well separated. A similar loss in resolution with the TCDF isomers has been noted by Swerev and Ballschmiter [54] for the SP-2331 phase although no new separations were reported.

Most of the 136 PCDDs and PCDFs can be readily separated from each other using a combination of conventional GC phases. Exceptions to this are certain pairs of PCDDs containing mostly 124-substitution. These are 1247/1248, 1246/1249, 12468/12479, 12467/12489, 124679/124689 and 123679/123689 for which there is little or no resolution on the common GC phases. However, the newly developed smectic liquid crystalline phase [36,37,41] is unique in its resolving powers and is readily capable of resolving to base line the above six PCDD pairs. In fact it has not been possible until the advent of this stationary phase to specify the relative proportions of these isomer pairs. The smectic crystalline phase appears to have other unusual properties. Our separations for the TCDDs differ from those of Mahle *et al.* [41] in

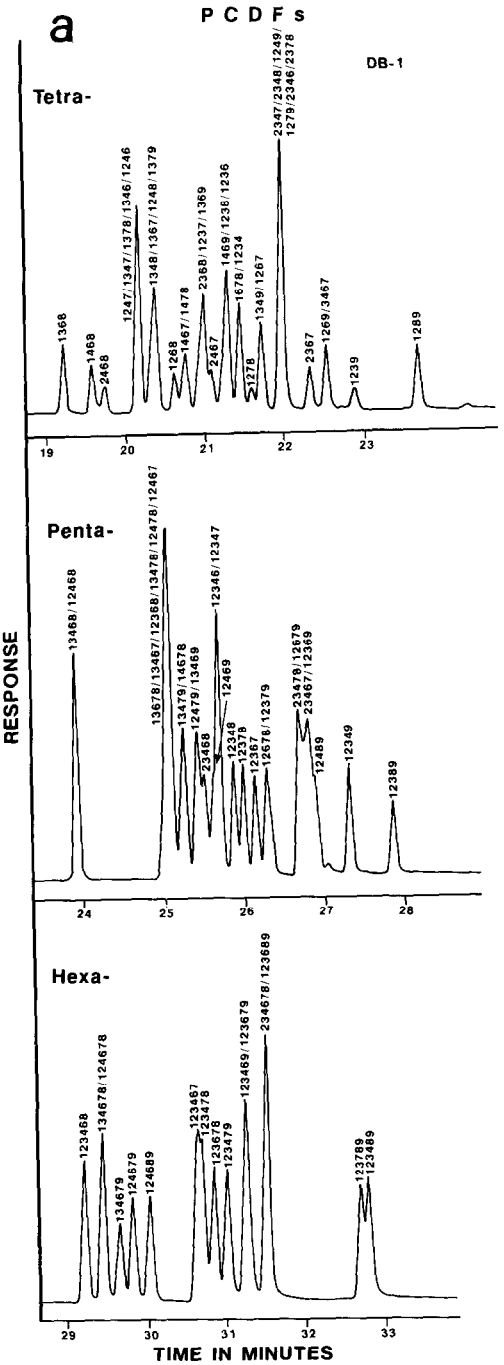
a
PCDFs
DB-1
Tetra-
1368
1468
2468
1247/1347/1378/1346/1246
1348/1367/1248/1379
1288
1467/1478
2368/1237/1369
2467
1469/1236/1236
1678/1234
1278
1349/1267
2347/2348/1249/
1279/2346/2378
2367
1269/3467
1239
1289
19
20
21
22
23
Penta-
13468/12468
13678/13467/12368/13478/12478/12467
13479/14678
12479/13468
23468
12469
12346/12347
12348
12378
12367
12678/12379
23478/12679
23467/12369
12489
12349
12389
24
25
26
27
28
Hexa-
123468
134678/124678
134679
124679
124689
123467
123478
123678
123479
123469/123679
234678/123689
123789
123489
29
30
31
32
33
RESPONSE
TIME IN MINUTES

Fig. 2.

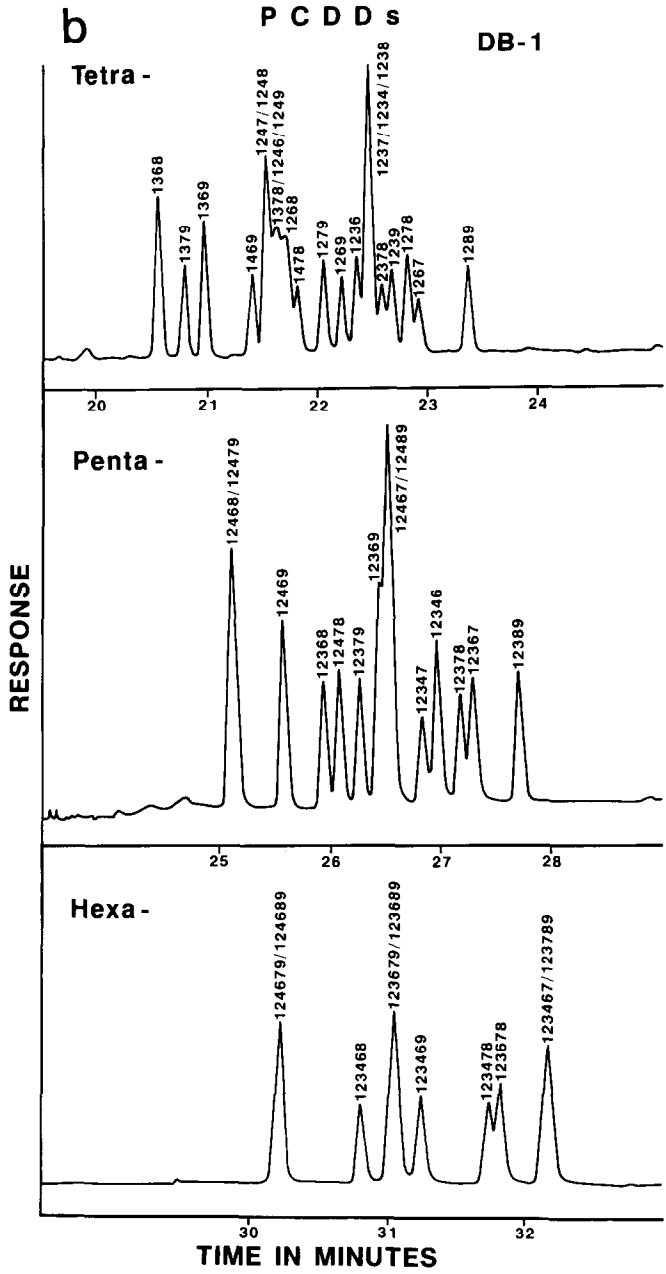

Fig. 2. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a DB-1 fused-silica bonded phase capillary column. (b) GC ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a DB-1 fused-silica bonded phase capillary column.

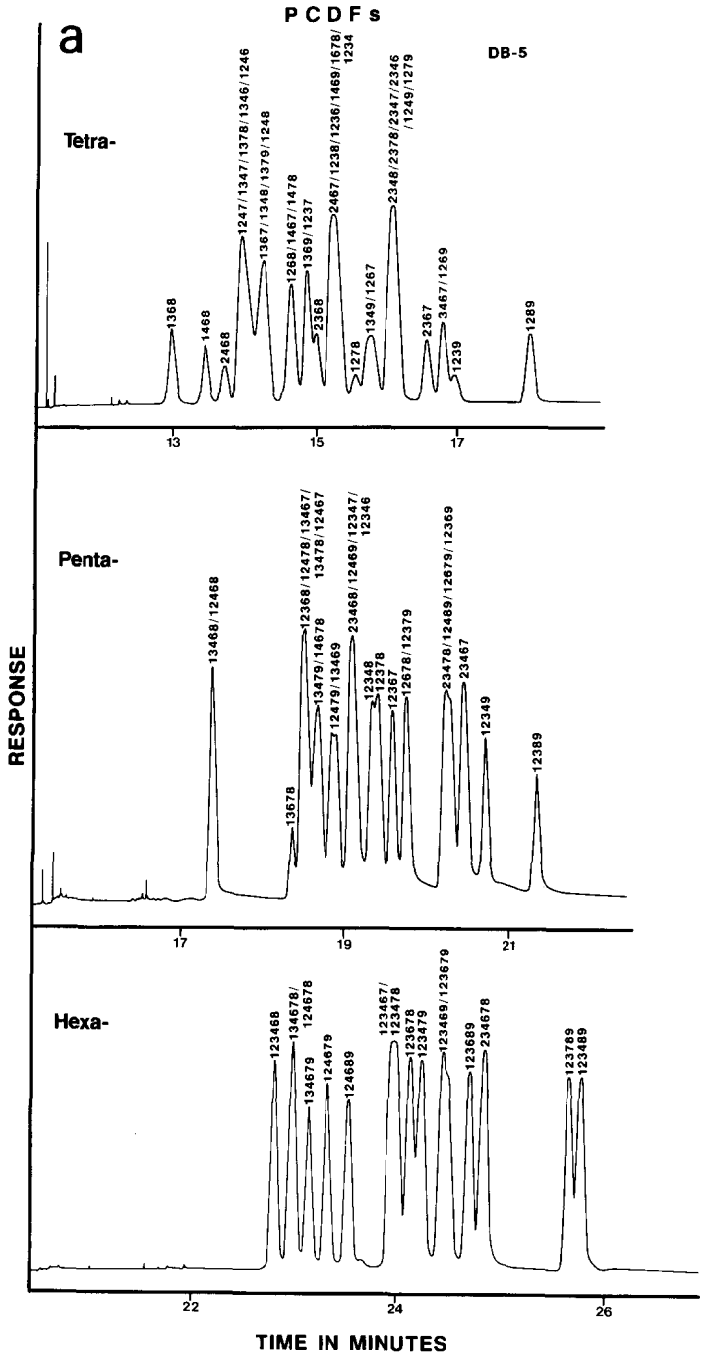
PCDFs
a
DB-5
Tetra-
1368
1468
2468
1247/1347/1378/1346/1246
1367/1348/1379/1248
1268/1467/1478
1369/1237
2368
2467/1238/1236/1469/1678/1234
1278
1349/1267
2348/2378/2347/2346/1249/1279
2367
3467/1269
1239
1289
13
15
17
Penta-
13468/12468
13678
12368/12478/13467/13478/12467
13479/14678
12479/13469
23468/12469/12347/12346
12348
12378
12367
12678/12379
23478/12489/12679/12369
23467
12349
12389
17
19
21
Hexa-
123468
134678/124678
134679
124679
124689
123467/123478
123678
123479
123469/123679
123689
234678
123789
123489
22
24
26
RESPONSE
TIME IN MINUTES

Fig. 3.

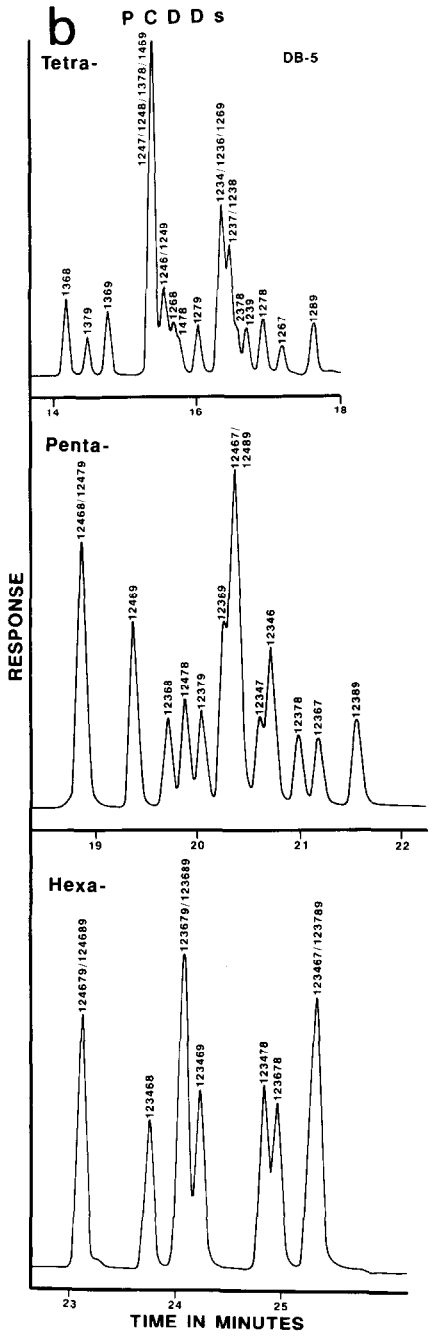

Fig. 3 (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a DB-5 fused-silica bonded phase capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a DB-5 fused-silica bonded phase capillary column.

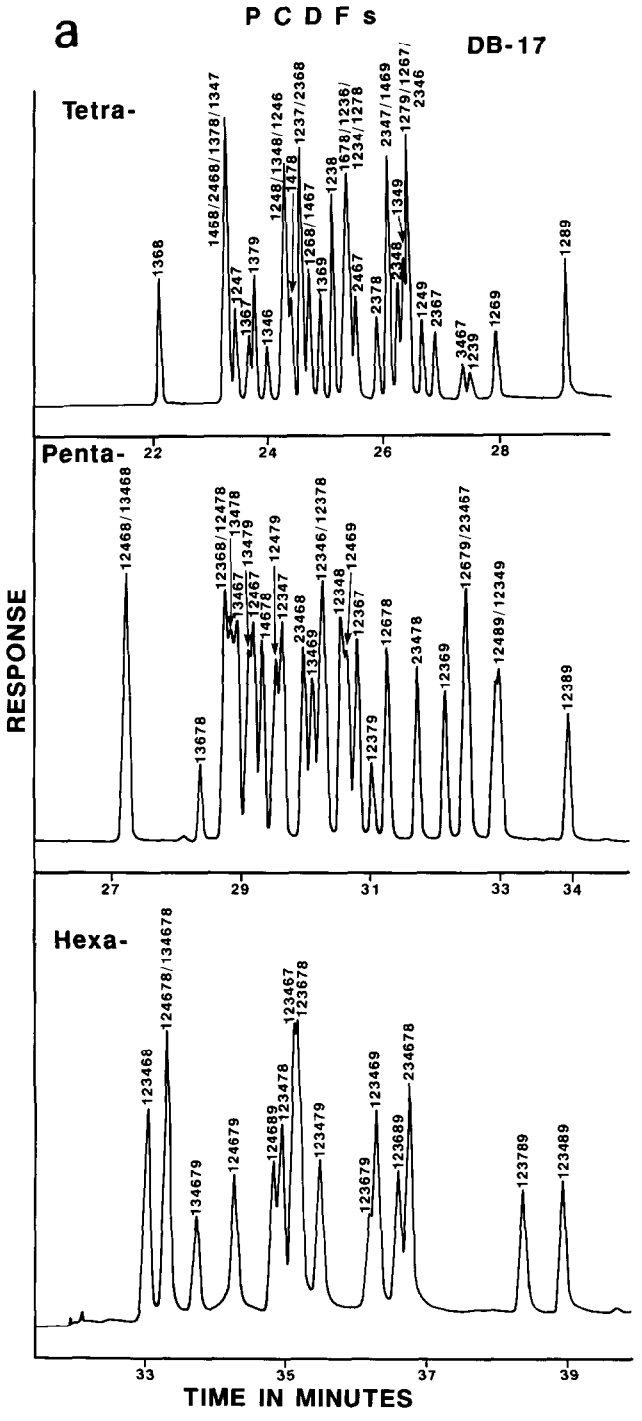
a
P C D F s
DB-17
Tetra-
1368
1468/2468/1378/1347
1247
1367
1379
1346
1248/1348/1246
1478
1237/2368
1268/1467
1369
1238
1678/1236/
1234/1278
2467
2378
2348
2347/1469
1349
1279/1267/
2346
1249
2367
3467
1239
1269
1289
Penta-
22
24
26
28
12468/13468
13678
12368/12478
13467
13478
12467
14678
13479
12479
12347
23468
13469
12346/12378
12348
12367
12469
12678
12379
23478
12369
12679/23467
12489/12349
12389
27
29
31
33
34
Hexa-
123468
124678/134678
134679
124679
124689
123478
123467
123678
123479
123679
123469
123689
234678
123789
123489
33
35
37
39
TIME IN MINUTES
RESPONSE

Fig. 4.

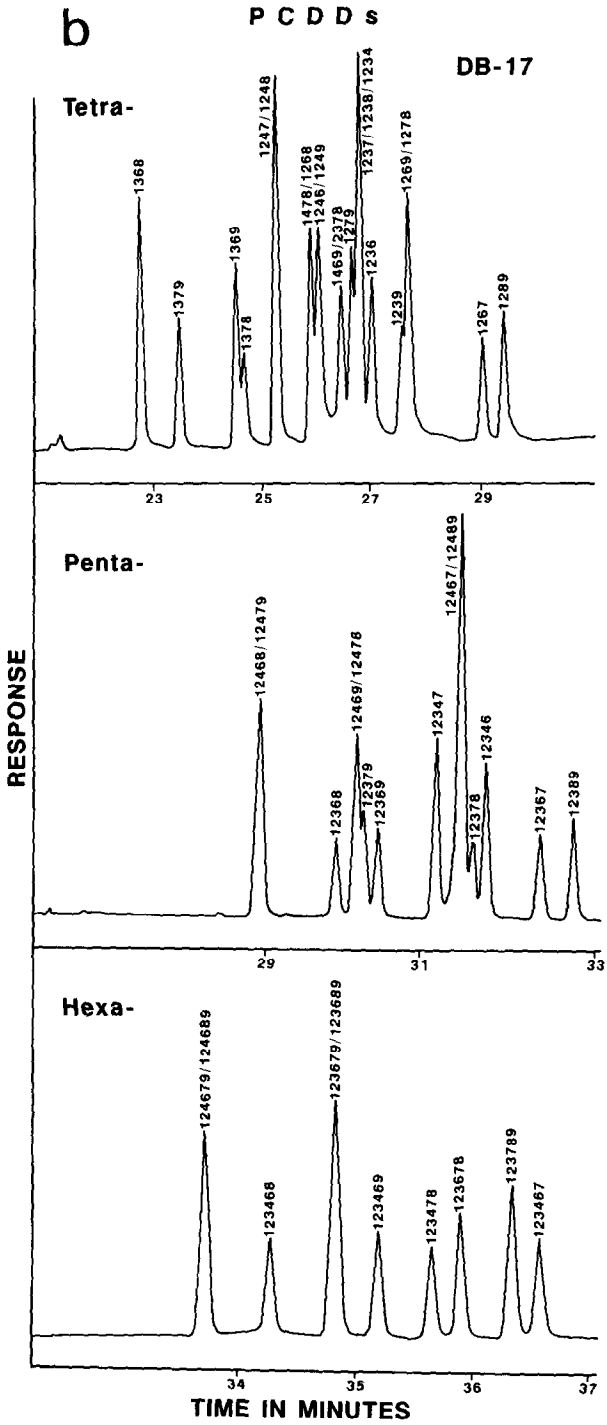

Fig. 4. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a DB-17 fused-silica bonded phase capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a DB-17 fused-silica bonded phase capillary column.

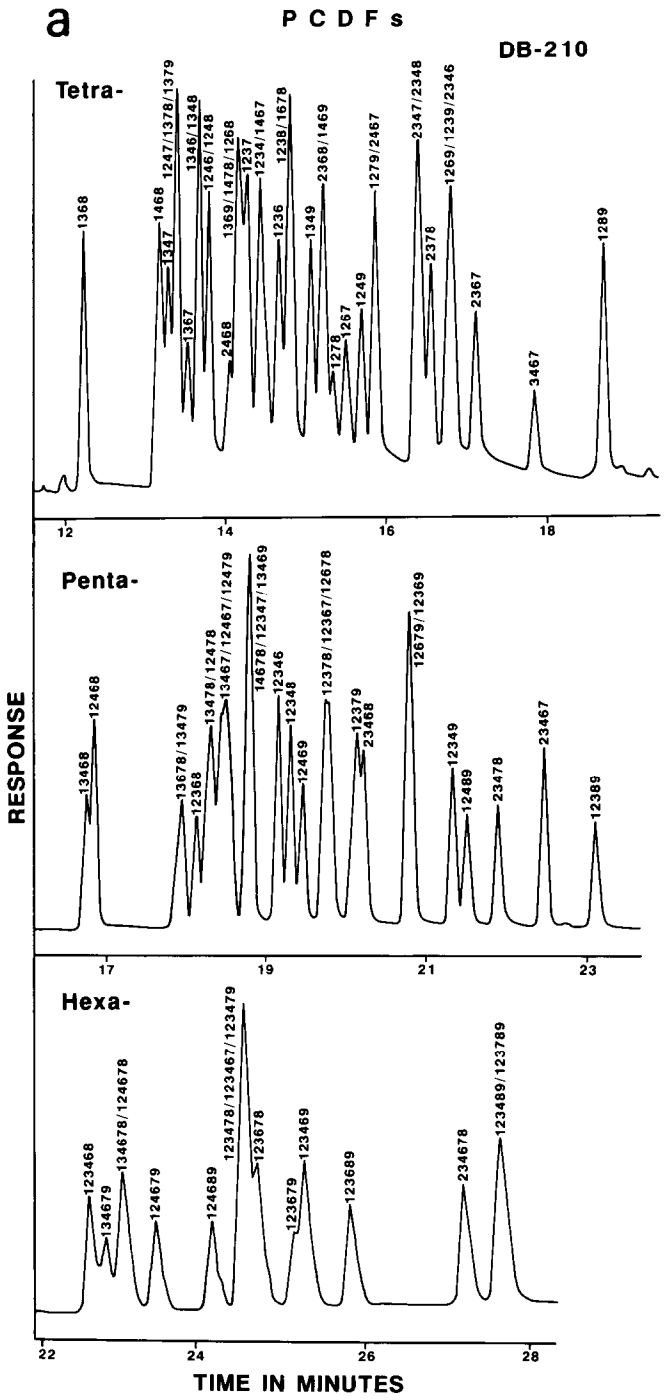
a
PCDFs
DB-210
Tetra-
1368
1468
1347
1247/1378/1379
1367
1346/1348
1246/1248
2468
1369/1478/1268
1237
1234/1467
1238/1678
1236
1349
2368/1469
1278
1267
1249
1279/2467
2347/2348
2378
1269/1239/2346
2367
3467
1289
12
14
16
18
Penta-
13468
12468
13678/13479
12368
13478/12478
13467/12467/12479
14678/12347/13469
12346
12348
12469
12378/12367/12678
12379
23468
12679/12369
12349
12489
23478
23467
12389
17
19
21
23
Hexa-
123468
134679
134678/124678
124679
124689
123478/123467/123479
123678
123679
123469
123689
234678
123489/123789
22
24
26
28
RESPONSE
TIME IN MINUTES

Fig. 5.

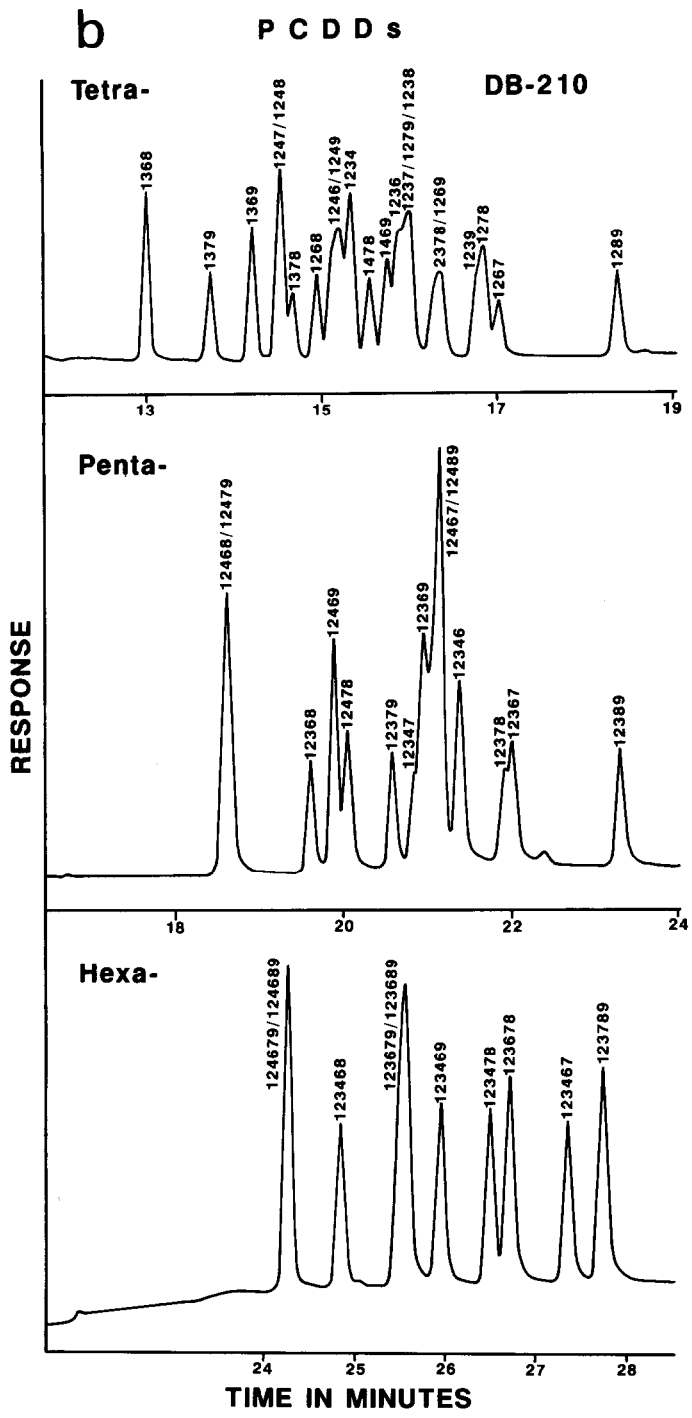

Fig. 5. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a DB-210 fused-silica bonded phase capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a DB-210 fused-silica bonded phase capillary column.

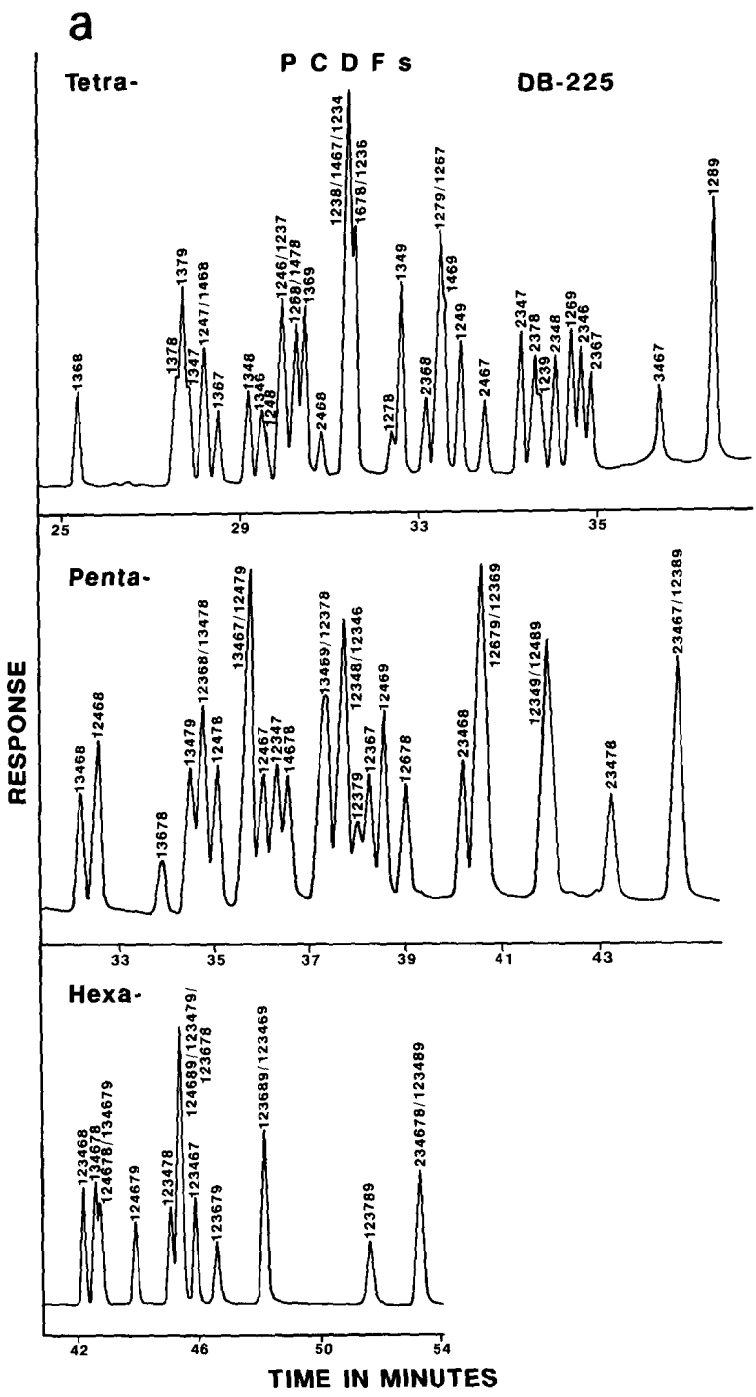
a
PCDFs
Tetra-
DB-225
1368
1378
1379
1347
1247/1468
1367
1348
1346
1248
1246/1237
1268/1478
1369
2468
1238/1467/1234
1678/1236
1278
1349
2368
1279/1267
1469
1249
2467
2347
2378
1239
2348
1269
2346
2367
3467
1289
25
29
33
35
Penta-
13468
12468
13678
13479
12368/13478
12478
13467/12479
12467
12347
14678
13469/12378
12348/12346
12379
12367
12469
12678
23468
12679/12369
12349/12489
23478
23467/12389
33
35
37
39
41
43
Hexa-
123468
123478
124678/134679
124679
123478
124689/123479/
123678
123467
123679
123689/123469
123789
234678/123489
42
46
50
54
RESPONSE
TIME IN MINUTES

Fig. 6.

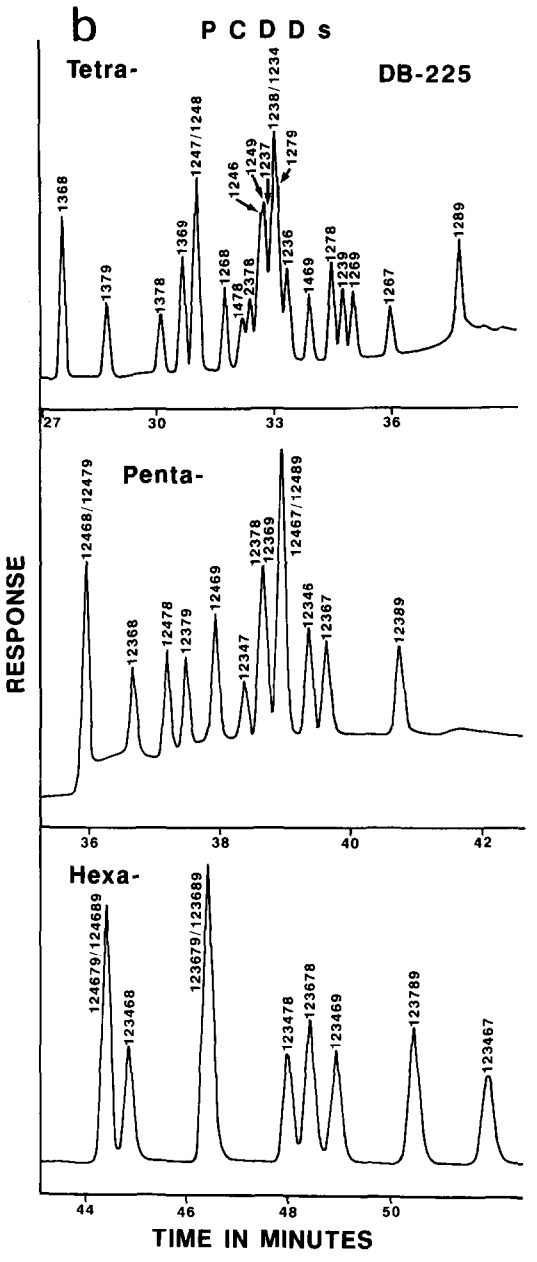

Fig. 6. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a DB-225 fused-silica bonded phase capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a DB-225 fused-silica bonded phase capillary column.

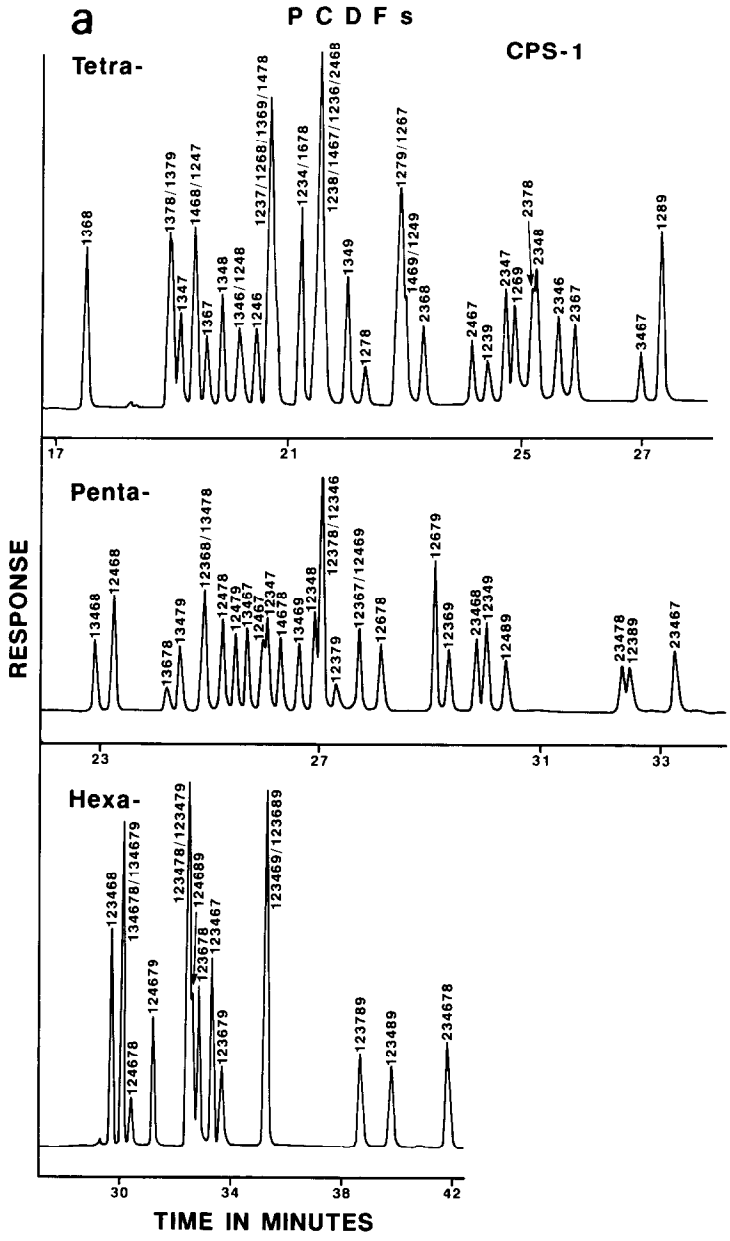
a
P C D F s
CPS-1
Tetra-
1368
1378/1379
1347
1468/1247
1367
1348
1346/1248
1246
1237/1268/1369/1478
1234/1678
1238/1467/1236/2468
1349
1278
1279/1267
1469/1249
2368
2467
1239
2347
1269
2378
2348
2346
2367
3467
1289
17
21
25
27
Penta-
13468
12468
13678
13479
12368/13478
12478
12479
13467
12467
12347
14678
13469
12348
12378/12346
12379
12367/12469
12678
12679
12369
23468
12349
12489
23478
12389
23467
23
27
31
33
Hexa-
123468
134678/134679
124679
124678
123478/123479
124689
123678
123467
123679
123469/123689
123789
123489
234678
30
34
38
42
RESPONSE
TIME IN MINUTES

Fig. 7.

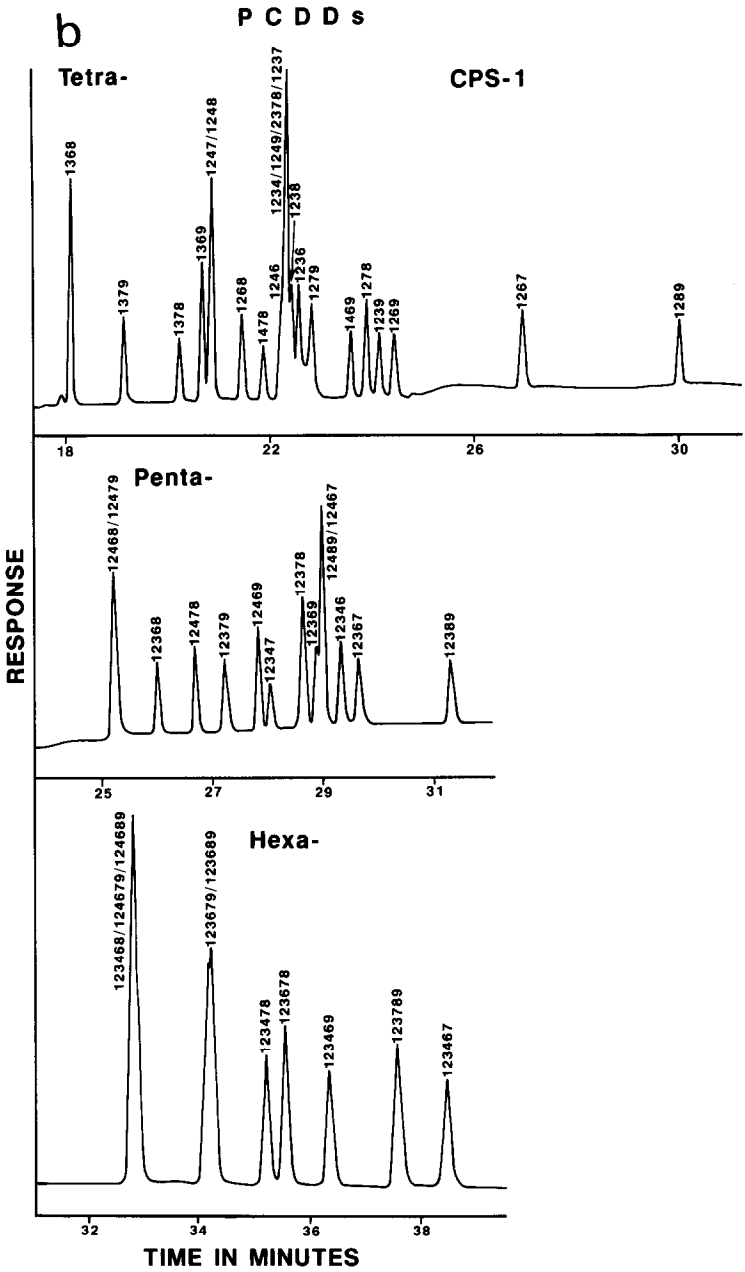

Fig. 7. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a CPS-1 fused-silica capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a CPS-1 fused-silica capillary column.

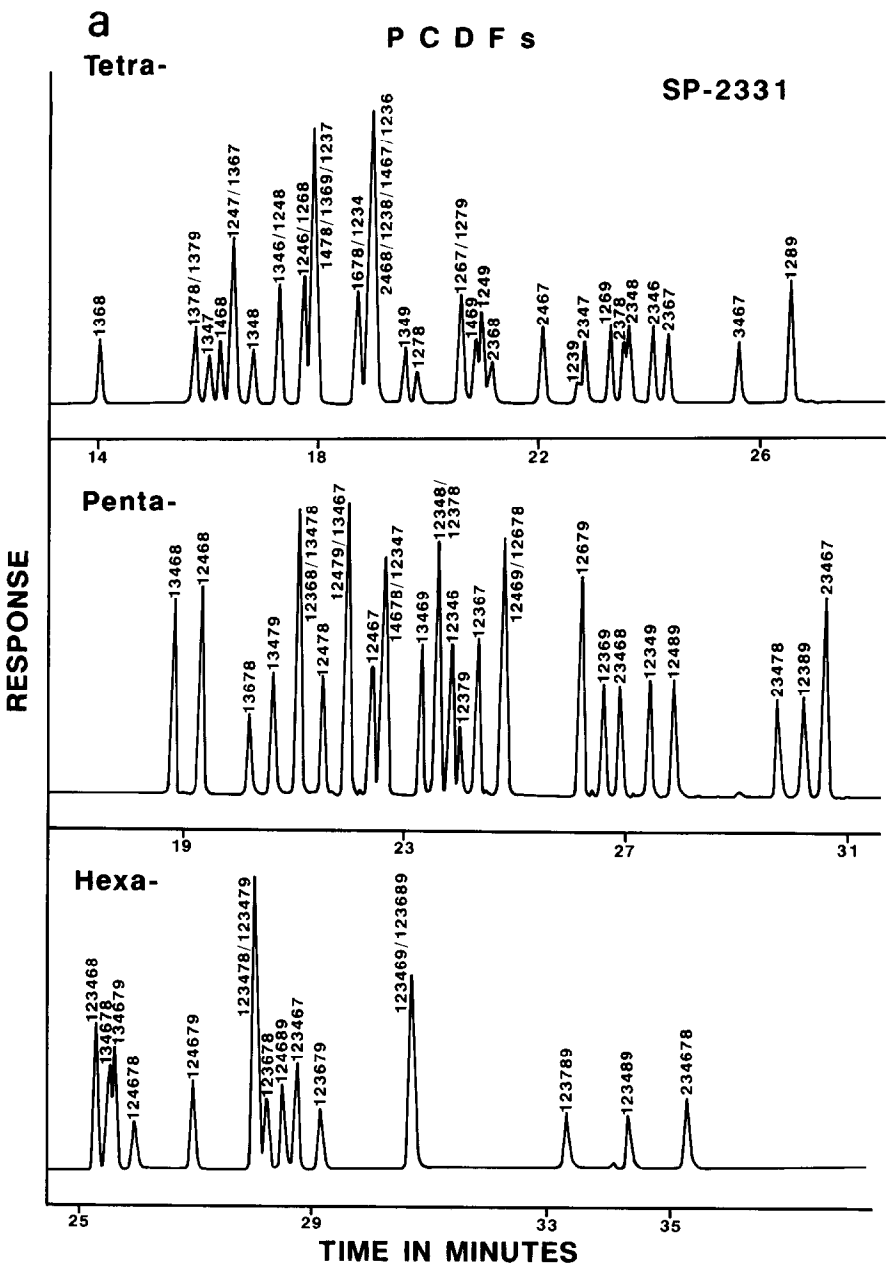
a
PCDFs
Tetra-
SP-2331
1368
1378/1379
1347
1468
1247/1367
1348
1346/1248
1246/1268
1478/1369/1237
1678/1234
2468/1238/1467/1236
1349
1278
1267/1279
1469
1249
2368
2467
1239
2347
1269
2378
2348
2346
2367
3467
1289
14
18
22
26
Penta-
13468
12468
13678
13479
12368/13478
12478
12479/13467
12467
14678/12347
13469
12348/12378
12346
12379
12367
12469/12678
12679
12369
23468
12349
12489
23478
12389
23467
19
23
27
31
Hexa-
123468
134678
134679
124678
124679
123478/123479
123678
124689
123467
123679
123469/123689
123789
123489
234678
25
29
33
35
RESPONSE
TIME IN MINUTES

Fig. 8.

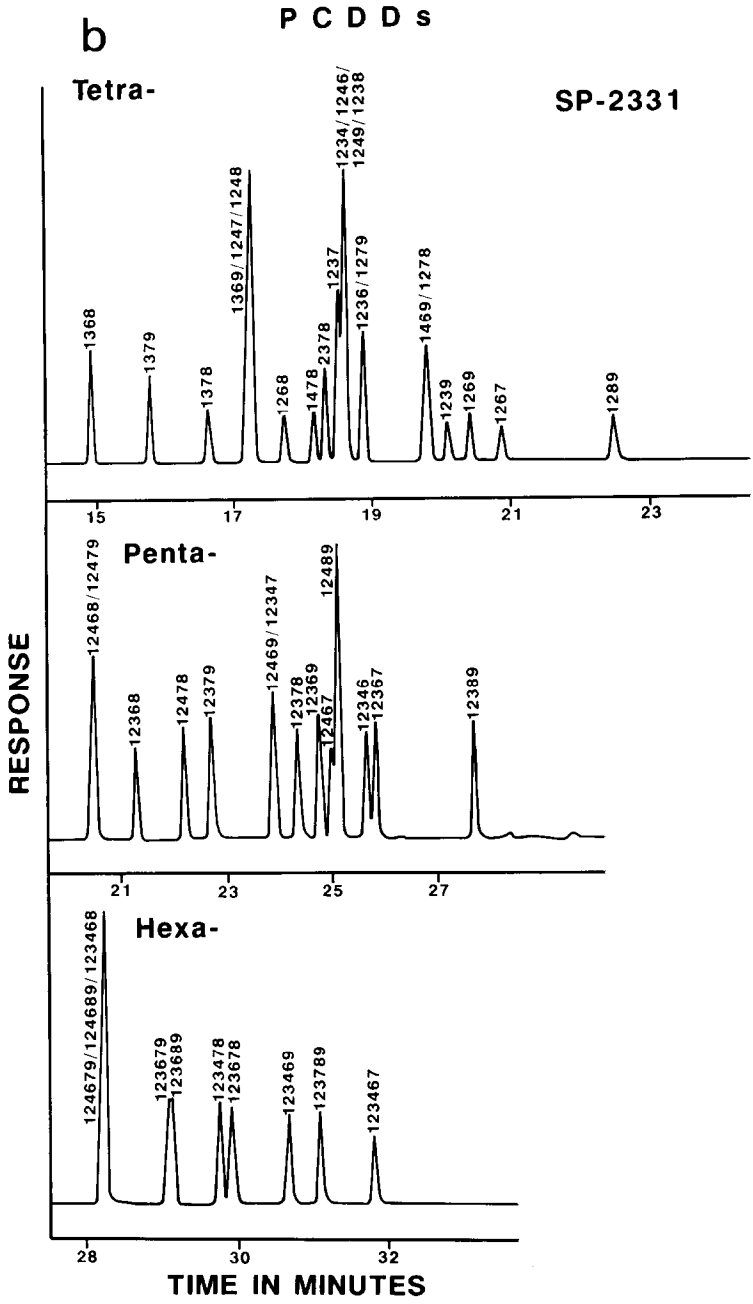

Fig. 8. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a SP-2331 fused-silica capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a SP-2331 fused-silica capillary column.

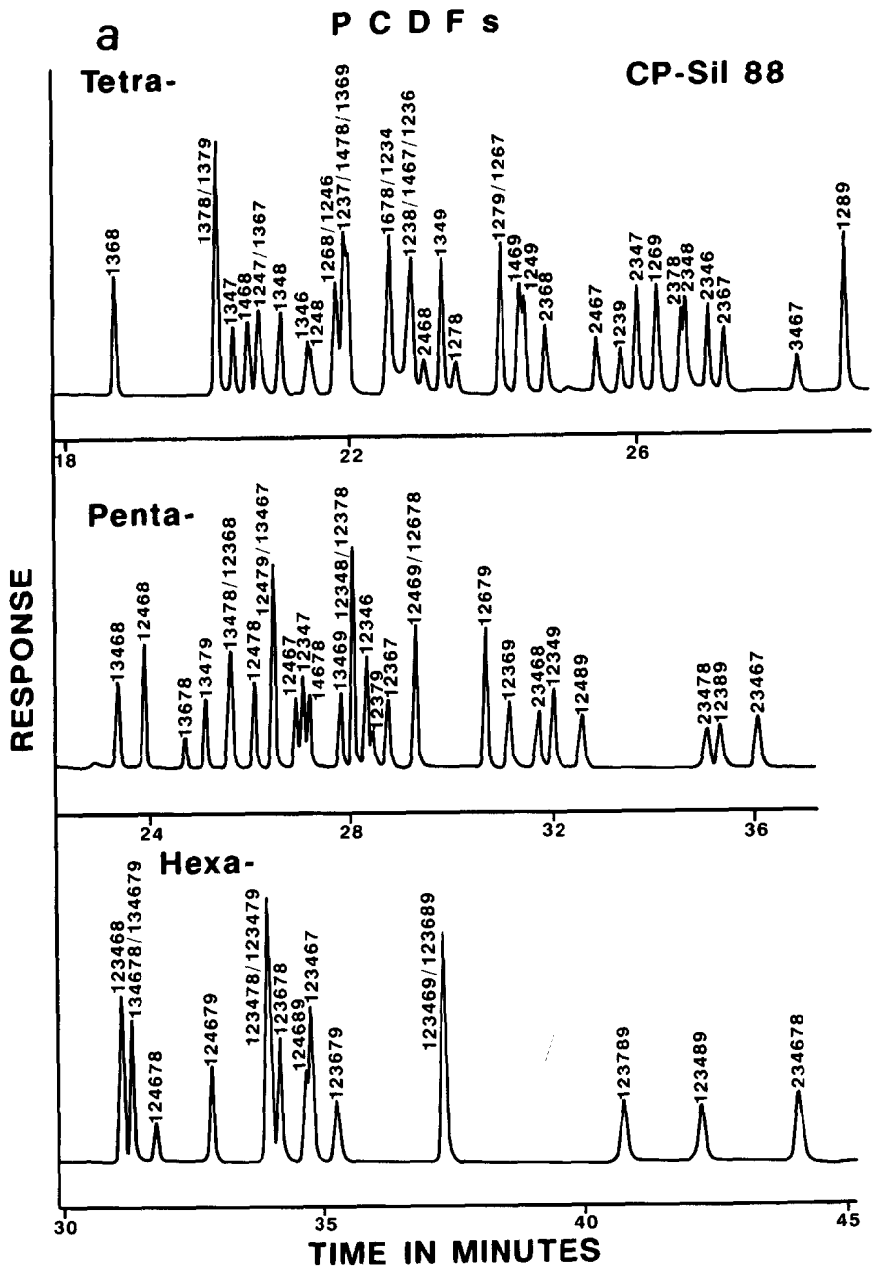
a
PCDFs
Tetra-
CP-Sil 88
1368
1378/1379
1347
1468
1247/1367
1348
1346
1248
1268/1246
1237/1478/1369
1678/1234
1238/1467/1236
2468
1278
1349
1279/1267
1469
1249
2368
2467
1239
2347
1269
2378
2348
2346
2367
3467
1289
18
22
26
Penta-
13468
12468
13678
13479
13478/12368
12478
12479/13467
12467
12347
14678
13469
12348/12378
12346
12379
12367
12469/12678
12679
12369
23468
12349
12489
23478
12389
23467
24
28
32
36
Hexa-
123468
134678/134679
124678
124679
123478/123479
123678
124689
123467
123679
123469/123689
123789
123489
234678
30
35
40
45
RESPONSE
TIME IN MINUTES

Fig. 9.

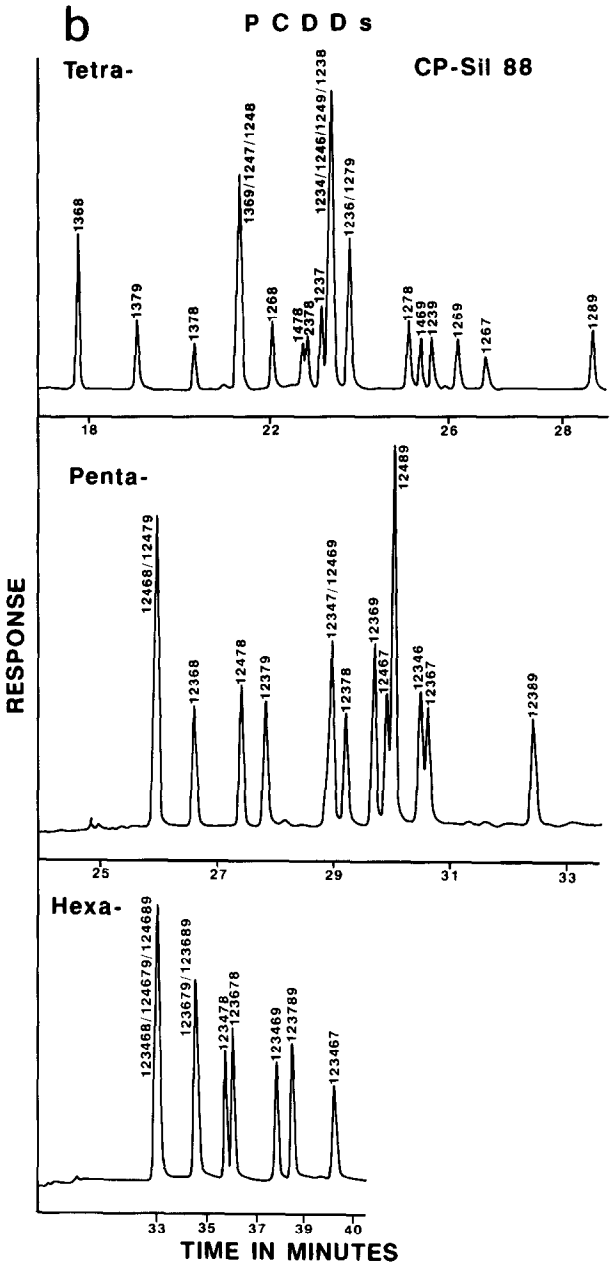

Fig. 9. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a CP-Sil 88 fused-silica capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a CP-Sil 88 fused-silica capillary column.

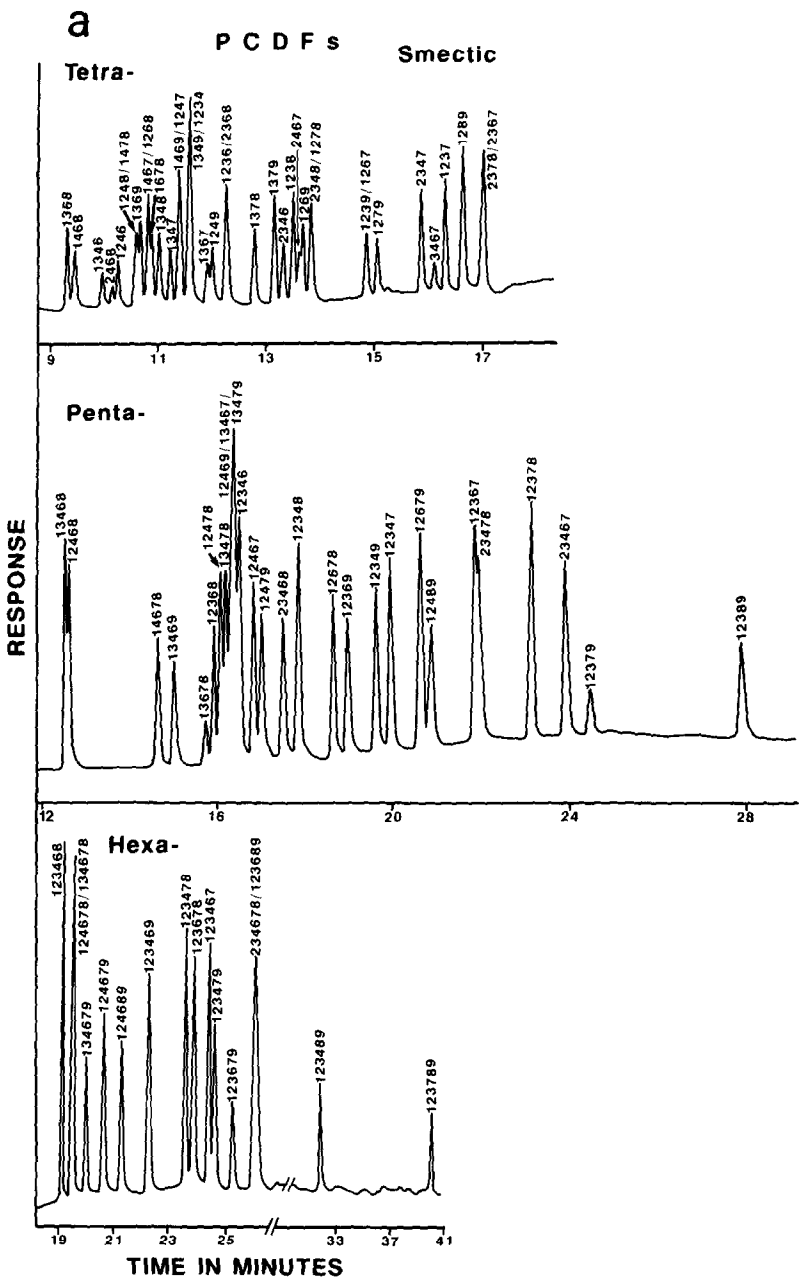
a
P C D F s
Smectic
Tetra-
1368
1468
1346
2468
1246
1248/1478
1369
1467/1268
1348
1678
1367
1469/1247
1349/1234
1249
1236/2368
1378
1379
2346
1238
2467
1269
2348/1278
1239/1267
1279
2347
3467
1237
1289
2378/2367
9
11
13
15
17
Penta-
RESPONSE
13468
12468
14678
13469
13678
12368
12478
13478
12469/13467/
13479
12346
12467
12479
23468
12348
12678
12369
12349
12347
12679
12489
12367
23478
12378
23467
12379
12389
12
16
20
24
28
Hexa-
123468
124678/134678
134679
124679
124689
123469
123478
123568
123467
123479
123679
234678/123689
123489
123789
19
21
23
25
33
37
41
TIME IN MINUTES

Fig. 10.

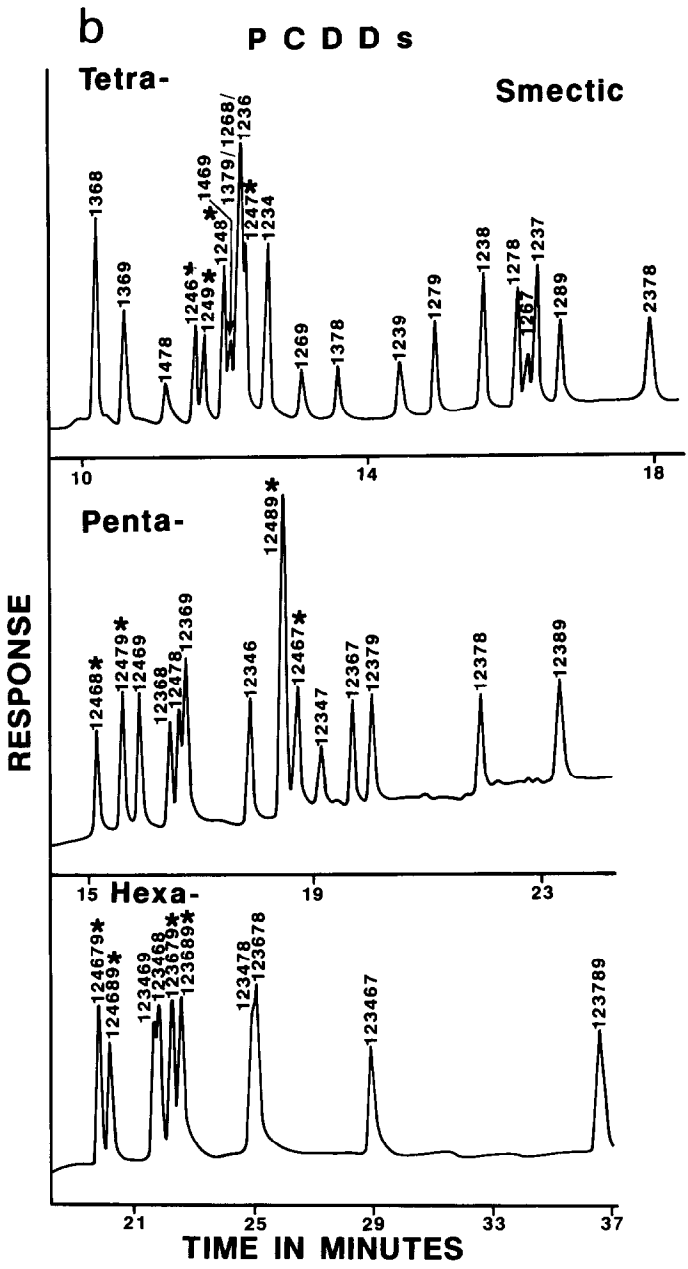

Fig. 10. (a) GC–ECD tracing of the separation of 38 TCDFs, 28 PnCDFs, and 16 HxCDFs on a liquid crystalline smectic fused-silica capillary column. (b) GC–ECD tracing of the separation of 22 TCDDs, 14 PnCDDs, and 10 HxCDDs on a liquid crystalline smectic fused-silica capillary column; congeners marked with an asterisk are pairs which cannot be unequivocably assigned (*cf.* text.).

TABLE V

GC RETENTION TIMES OF PCDF/PCDD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A DB-1 FUSED-SILICA BONDED PHASE CAPILLARY COLUMN

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF[a]					
1	1368	1.000	20	1469	1.091
2	1468	1.016	21	1238	1.091
3	2468	1.023	22	1236	1.091
4	1247	1.041	23	1678	1.099
5	1347	1.041	24	1234	1.099
6	1378	1.041	25	1278	1.105
7	1346	1.041	26	1349	1.111
8	1246	1.041	27	1267	1.111
9	1348	1.051	28	2347	1.122
10	1367	1.051	29	2348	1.122
11	1248	1.051	30	1249	1.122
12	1379	1.051	31	1279	1.122
13	1268	1.062	32	2346	1.122
14	1467	1.068	33	2378	1.122
15	1478	1.068	34	2367	1.138
16	2368	1.078	35	1269	1.147
17	1237	1.078	36	3467	1.147
18	1369	1.078	37	1239	1.162
19	2467	1.082	38	1289	1.198
–	13468-PnCDF	1.232	–	123468-HxCDF	1.513
–	1368-TCDD	1.056			
PnCDF[b]					
1	13468	1.000	15	12346	1.074
2	12468	1.000	16	12347	1.074
3	13678	1.048	17	12348	1.082
4	13467	1.048	18	12378	1.087
5	12368	1.048	19	12367	1.093
6	13478	1.048	20	12678	1.099
7	12478	1.048	21	12379	1.099
8	12467	1.048	22	23478	1.116
9	13479	1.056	23	12679	1.116
10	14678	1.056	24	23467	1.121
11	12479	1.063	25	12369	1.121
12	13469	1.063	26	12489	1.125
13	23468	1.067	27	12349	1.142
14	12469	1.071	28	12389	1.164
HxCDF[c]					
1	123468	1.000	9	123678	1.048
2	134678	1.007	10	123479	1.053
3	124678	1.007	11	123469	1.060
4	134679	1.013	12	123679	1.060
5	124679	1.018	13	234678	1.067
6	124689	1.024	14	123689	1.067
7	123467	1.042	15	123789	1.102
8	123478	1.043	16	123489	1.105

TABLE V *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD[d]					
1	1368	1.000	12	1279	1.075
2	1379	1.012	13	1269	1.084
3	1369	1.021	14	1236	1.091
4	1469	1.043	15	1237	1.096
5	1247	1.050	16	1234	1.096
6	1248	1.050	17	1238	1.096
7	1378	1.054	18	2378	1.103
8	1246	1.054	19	1239	1.107
9	1249	1.054	20	1278	1.114
10	1268	1.058	21	1267	1.118
11	1478	1.064	22	1289	1.142
–	12468-PnCDD	1.233	–	124679-HxCDD	1.469
–	1368-TCDF	0.947			
PnCDD[e]					
1	12468	1.000	8	12467	1.054
2	12479	1.000	9	12489	1.054
3	12469	1.018	10	12347	1.067
4	12368	1.032	11	12346	1.072
5	12478	1.038	12	12378	1.080
6	12379	1.045	13	12367	1.084
7	12369	1.052	14	12389	1.100
HxCDD[f]					
1	124679	1.000	6	123469	1.037
2	124689	1.000	7	123478	1.054
3	123468	1.021	8	123678	1.057
4	123679	1.030	9	123467	1.069
5	123689	1.030	10	123789	1.069

[a] RT reference standard is 1368-TCDF.
[b] RT reference standard is 13468-PnCDF.
[c] RT reference standard is 123468-HxCDF.
[d] RT reference standard is 1368-TCDD.
[e] RT reference standard is 12468-PnCDD.
[f] RT reference standard is 124679-HxCDD.

some of the elution orders. In this respect Richle *et al.* [37] have noticed that the retention times and even relative elution orders of the PCDDs/PCDFs on various smectic columns changed according to the thermal history of the column. This enigmatic property of the smectic phase may explain the different reported elution orders.

Thus for any sample containing mixtures of PCDDs and PCDFs, it is possible to assign the exact isomeric configuration of any peak except the six pairs noted provided two or more GC columns are used. For samples such as fly ash, waste material or PCB extracts, many congeners will be present and probably more than two GC columns would be necessary for detailed specific identification. This data would also be useful in the selection of stationary phases for use in dual or multi-dimensional GC [21,55].

TABLE VI

GC RETENTION TIMES OF PCDF/PCDD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A DB-5 FUSED-SILICA BONDED PHASE CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1238	1.122
2	1468	1.025	21	1236	1.122
3	2468	1.040	22	1469	1.122
4	1247	1.053	23	1678	1.122
5	1347	1.053	24	1234	1.122
6	1378	1.053	25	1278	1.139
7	1346	1.053	26	1349	1.151
8	1246	1.053	27	1267	1.151
9	1367	1.069	28	2348	1.168
10	1348	1.069	29	2378	1.168
11	1379	1.069	30	2347	1.168
12	1248	1.069	31	2346	1.168
13	1268	1.090	32	1249	1.168
14	1467	1.090	33	1279	1.168
15	1478	1.090	34	2367	1.193
16	1369	1.102	35	3467	1.205
17	1237	1.102	36	1269	1.205
18	2368	1.109	37	1239	1.214
19	2467	1.122	38	1289	1.271
–	13468-PnCDF	1.298	–	123468-HxCDF	1.667
–	1368-TCDD	1.073			
PnCDF					
1	13468	1.000	15	12347	1.093
2	12468	1.000	16	12346	1.093
3	13678	1.053	17	12348	1.107
4	12368	1.061	18	12378	1.110
5	12478	1.061	19	12367	1.120
6	13467	1.061	20	12678	1.129
7	13478	1.061	21	12379	1.129
8	12467	1.061	22	23478	1.156
9	13479	1.070	23	12489	1.156
10	14678	1.070	24	12679	1.156
11	12479	1.080	25	12369	1.156
12	13469	1.082	26	23467	1.167
13	23468	1.093	27	12349	1.182
14	12469	1.093	28	12389	1.216
HxCDF					
1	123468	1.000	9	123678	1.061
2	134678	1.008	10	123479	1.066
3	124678	1.008	11	123469	1.078
4	134679	1.016	12	123679	1.078
5	124679	1.024	13	123689	1.088
6	124689	1.034	14	234678	1.095
7	123467	1.052	15	123789	1.133
8	123478	1.056	16	123489	1.138

TABLE VI *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	1279	1.102
2	1379	1.016	13	1234	1.120
3	1369	1.032	14	1236	1.120
4	1247	1.066	15	1269	1.120
5	1248	1.066	16	1237	1.126
6	1378	1.066	17	1238	1.126
7	1469	1.066	18	2378	1.131
8	1246	1.075	19	1239	1.139
9	1249	1.075	20	1278	1.152
10	1268	1.083	21	1267	1.166
11	1478	1.088	22	1289	1.191
–	12468-PnCDD	1.298	–	124679-HxCDD	1.603
–	1368-TCDF	0.932			
PnCDD					
1	12468	1.000	8	12467	1.073
2	12479	1.000	9	12489	1.073
3	12469	1.025	10	12347	1.085
4	12368	1.041	11	12346	1.090
5	12478	1.049	12	12378	1.103
6	12379	1.057	13	12367	1.112
7	12369	1.068	14	12389	1.130
HxCDD					
1	124679	1.000	6	123469	1.045
2	124689	1.000	7	123478	1.070
3	123468	1.026	8	123678	1.075
4	123679	1.039	9	123467	1.090
5	123689	1.039	10	123789	1.090

Comparison to published reports

The data generated in this report is a confirmation of much previous work and agrees in all respects with that reported in the literature except for the following.

TCDDs. Taylor *et al.* [23] of Wright State University noted a difference between their work and two earlier reports [10,11] in the elution order of three TCDDs, 1268-, 1278- and 1279-TCDD, on both a DB-5 and SP-2331 columns and were unable to distinguish the correct elution order. Subsequently Gurka *et al.* [56], Gelbaum *et al.* [30] and Donnelly *et al.* [34] all investigated these elution orders and agreed with the elution order of Buser and Rappe [11]. We also find the same elution order as did Buser and Rappe [11]. Harden *et al.* [40] reported further separations of all 22 TCDDs and all 38 TCDFs on 4 additional GC phases including 3 in this report (DB-225, SP-2401 equivalent to DB-210, and SP-2250 equivalent to DB-17). While we are in complete agreement with their TCDF assignments, we differ markedly for those on the 1268-, 1278-, and 1279-TCDD isomers and suspect they may have used the earlier Dow assignment [10] rather than that of Buser and Rappe [11] which we and others believe to be correct.

TABLE VII

GC RETENTION TIMES OF PCDF/PCDD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A DB-17 FUSED-SILICA BONDED PHASE CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1678	1.156
2	1468	1.056	21	1236	1.156
3	2468	1.056	22	1234	1.156
4	1378	1.056	23	1278	1.156
5	1347	1.056	24	2467	1.163
6	1247	1.063	25	2378	1.180
7	1367	1.074	26	2347	1.189
8	1379	1.078	27	1469	1.189
9	1346	1.089	28	2348	1.196
10	1248	1.103	29	1349	1.202
11	1348	1.105	30	1279	1.205
12	1246	1.105	31	1267	1.205
13	1478	1.109	32	2346	1.205
14	1237	1.118	33	1249	1.217
15	2368	1.118	34	2367	1.228
16	1268	1.124	35	3467	1.250
17	1467	1.124	36	1239	1.256
18	1369	1.134	37	1269	1.278
19	1238	1.114	38	1289	1.336
–	13468-PnCDF	1.235	–	123468-HxCDF	1.493
–	1368-TCDD	1.053			
PnCDF					
1	12468	1.000	15	12346	1.101
2	13468	1.000	16	12378	1.103
3	13678	1.039	17	12348	1.114
4	12368	1.052	18	12469	1.117
5	12478	1.052	19	12367	1.122
6	13478	1.055	20	12379	1.130
7	13467	1.058	21	12678	1.138
8	13479	1.063	22	23478	1.155
9	12467	1.067	23	12369	1.169
10	14678	1.072	24	12679	1.180
11	12479	1.079	25	23467	1.180
12	12347	1.082	26	12489	1.197
13	23468	1.095	27	12349	1.197
14	13469	1.098	28	12389	1.233
HxCDF					
1	123468	1.000	9	123678	1.055
2	124678	1.007	10	123479	1.064
3	134678	1.007	11	123679	1.082
4	134679	1.018	12	123469	1.085
5	124679	1.033	13	123689	1.093
6	124689	1.047	14	234678	1.097
7	123478	1.050	15	123789	1.139
8	123467	1.052	16	123489	1.154

TABLE VII *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.00	12	2378	1.123
2	1379	1.024	13	1279	1.129
3	1369	1.059	14	1237	1.134
4	1378	1.064	15	1238	1.134
5	1247	1.084	16	1234	1.136
6	1248	1.084	17	1236	1.142
7	1478	1.104	18	1239	1.161
8	1268	1.104	19	1269	1.164
9	1246	1.109	20	1278	1.164
10	1249	1.109	21	1267	1.210
11	1469	1.123	22	1289	1.223
–	12468-PnCDD	1.235	–	124679-HxCDD	1.450
–	1368-TCDF	0.950			
PnCDD					
1	12468	1.000	8	12347	1.079
2	12479	1.000	9	12467	1.089
3	12368	1.034	10	12489	1.089
4	12469	1.042	11	12378	1.095
5	12478	1.042	12	12346	1.100
6	12379	1.045	13	12367	1.124
7	12369	1.052	14	12389	1.139
HxCDD					
1	124679	1.000	6	123469	1.049
2	124689	1.000	7	123478	1.064
3	123468	1.018	8	123678	1.072
4	123679	1.037	9	123789	1.086
5	123689	1.037	10	123467	1.094

With regard to the isomer pair, 1246/1249-TCDD, we readily separate them on HPLC using an ODS packing and a 5% water in methanol eluent, but O'Keefe *et al.* [14], Taylor *et al.* [23] and Wagel *et al.* [57] all reported no such separation. Moreover, we are unable to separate these two isomers on the polar CP-Sil 88 phase even though both Zoller and Ballschmiter [32] and Gelbaum *et al.* [30] achieved a small separation on that column. There is some degree of separation (20–30%) for this pair of TCDD isomers on the CPS-1 and DB-210 columns and a clear resolution on the liquid crystalline smectic.

The isomer pairs, 1237/1238-TCDD, from the Smiles rearrangement are not easy to separate and even more difficult to assign their structures using conventional means. We are unable to obtain significant GC separations of this pair on the first four GC phases listed in Table IV but do obtain almost 100% resolution on the other five phases (four of them being cyanopropyl and one the smectic). Because of our photolytic experiments with 12389-PnCDD and 12367-PnCDD, we assign 1237-TCDD and 1238-TCDD as the earlier and later eluters, respectively, on the cyanopropyl GC phases. On the other hand, the elution order on the smectic phase and

TABLE VIII

GC RETENTION TIMES OF PCDF/PCCD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A DB-210 FUSED-SILICA BONDED PHASE CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1238	1.212
2	1468	1.077	21	1678	1.212
3	1347	1.086	22	1349	1.233
4	1247	1.095	23	2368	1.245
5	1378	1.095	24	1469	1.245
6	1379	1.095	25	1278	1.256
7	1367	1.106	26	1267	1.269
8	1346	1.118	27	1249	1.285
9	1348	1.118	28	1279	1.299
10	1246	1.128	29	2467	1.299
11	1248	1.128	30	2347	1.342
12	2468	1.149	31	2348	1.342
13	1369	1.158	32	2378	1.355
14	1478	1.158	33	1269	1.375
15	1268	1.158	34	1239	1.375
16	1237	1.167	35	2346	1.375
17	1234	1.180	36	2367	1.401
18	1467	1.180	37	3467	1.461
19	1236	1.199	38	1289	1.530
–	13468-PnCDF	1.381	–	123468-HxCDF	1.858
–	1368-TCDD	1.084			
PnCDF					
1	13468	1.000	15	12348	1.151
2	12468	1.005	16	12469	1.160
3	13678	1.070	17	12378	1.178
4	13479	1.070	18	12367	1.178
5	12368	1.081	19	12678	1.180
6	13478	1.092	20	12379	1.202
7	12478	1.092	21	23468	1.205
8	13467	1.100	22	12679	1.239
9	12467	1.103	23	12369	1.239
10	12479	1.103	24	12349	1.271
11	14678	1.121	25	12489	1.281
12	12347	1.121	26	23478	1.304
13	13469	1.121	27	23467	1.338
14	12346	1.142	28	12389	1.376
HxCDF					
1	123468	1.000	9	123479	1.085
2	134679	1.009	10	123678	1.092
3	134678	1.018	11	123679	1.113
4	124678	1.018	12	123469	1.118
5	124679	1.036	13	123689	1.143
6	124689	1.067	14	234678	1.206
7	123478	1.085	15	123489	1.226
8	123467	1.085	16	123789	1.226

TABLE VIII *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	1469	1.196
2	1379	1.053	13	1236	1.205
3	1369	1.087	14	1237	1.209
4	1247	1.109	15	1279	1.211
5	1248	1.109	16	1238	1.211
6	1378	1.120	17	2378	1.237
7	1268	1.139	18	1269	1.241
8	1246	1.154	19	1239	1.266
9	1249	1.158	20	1278	1.273
10	1234	1.166	21	1267	1.287
11	1478	1.182	22	1289	1.383
–	12468-PnCDD	1.415	–	124679-HxCDD	1.840
–	1368-TCDF	0.923			
PnCDD					
1	12468	1.000	8	12369	1.113
2	12479	1.000	9	12467	1.122
3	12368	1.048	10	12489	1.122
4	12469	1.061	11	12346	1.133
5	12478	1.069	12	12378	1.156
6	12379	1.095	13	12367	1.164
7	12347	1.102	14	12389	1.225
HxCDD					
1	124679	1.000	6	123469	1.068
2	124689	1.000	7	123478	1.089
3	123468	1.024	8	123678	1.098
4	123679	1.052	9	123467	1.123
5	123689	1.052	10	123789	1.139

on RP-HPLC is reversed *i.e.* 1238-TCDD first followed by 1237-TCDD. In this regard we do not agree with the separations of Brown *et al.* [44] on DB-225 for 1234-, 1237- and 1238-TCDD. However column differences may account for some of this incompatability. Lastly, in this report and that of Buser and Rappe [17], the elution of 1239-TCDD on OV-1 is subsequent to that of 2378-TCDD whereas it was given by Oehme and Kirschmer [18] as preceding 2378-TCDD.

PnCDDs and HxCDDs. We can find no significant differences that have not already been noticed between our results and those reported previously for the above two homologues.

TCDFs. The early pioneering work by Mazer and co-workers [15,16] on this homologue and by Bell and Gara [22] on all PCDFs resulted in a comprehensive data base on their GC properties on methyl silicone (SE-54 equivalent to DB-5) and the SP-2330 phase (cyanopropyl). Mazer *et al.* [15] made two corrections to their list (ref. 15, p. 1648), one for 1236-TCDF on SE-54 and one for 2368-TCDF on SP-2330, both of which we are in agreement. Bell and Gara [22] also reported for the 1246-TCDF

TABLE IX

GC RETENTION TIMES OF PCDF/PCDD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A DB-225 FUSED SILICA BONDED PHASE CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1678	1.207
2	1378	1.073	21	1236	1.207
3	1379	1.078	22	1278	1.235
4	1347	1.084	23	1349	1.242
5	1247	1.095	24	2368	1.261
6	1468	1.095	25	1279	1.271
7	1367	1.106	26	1267	1.271
8	1348	1.128	27	1469	1.275
9	1346	1.139	28	1249	1.287
10	1248	1.142	29	2467	1.305
11	1246	1.154	30	2347	1.331
12	1237	1.154	31	2378	1.342
13	1268	1.164	32	1239	1.347
14	1478	1.164	33	2348	1.357
15	1369	1.170	34	1269	1.369
16	2468	1.183	35	2346	1.377
17	1238	1.202	36	2367	1.384
18	1467	1.202	37	3467	1.435
19	1234	1.202	38	1289	1.475
–	13468-PnCDF	1.298	–	123468-HxCDF	1.642
–	1368-TCDD	1.065			
PnCDF					
1	13468	1.000	15	12348	1.139
2	12468	1.009	16	12346	1.139
3	13678	1.044	17	12379	1.148
4	13479	1.058	18	12367	1.153
5	12368	1.065	19	12469	1.161
6	13478	1.065	20	12678	1.173
7	12478	1.073	21	23468	1.203
8	13467	1.089	22	12679	1.212
9	12479	1.089	23	12369	1.212
10	12467	1.097	24	12349	1.248
11	12347	1.105	25	12489	1.248
12	14678	1.110	26	23478	1.282
13	13469	1.128	27	23467	1.317
14	12378	1.131	28	12389	1.317
HxCDF					
1	123468	1.000	9	123678	1.081
2	134678	1.010	10	123467	1.093
3	124678	1.015	11	123679	1.112
4	134679	1.015	12	123689	1.152
5	124679	1.043	13	123469	1.152
6	123478	1.073	14	123789	1.240
7	124689	1.081	15	234678	1.282
8	123479	1.081	16	123489	1.282

TABLE IX *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	1237	1.178
2	1379	1.039	13	1238	1.184
3	1378	1.086	14	1234	1.184
4	1369	1.105	15	1279	1.189
5	1247	1.117	16	1236	1.196
6	1248	1.117	17	1469	1.215
7	1268	1.142	18	1278	1.234
8	1478	1.157	19	1239	1.244
9	2378	1.164	20	1269	1.254
10	1246	1.171	21	1267	1.286
11	1249	1.175	22	1289	1.346
–	12468-PnCDD	1.314	–	124679-HxCDD	1.639
–	1368-TCDF	0.939			
PnCDD					
1	12468	1.000	8	12369	1.104
2	12479	1.000	9	12378	1.105
3	12368	1.028	10	12467	1.115
4	12478	1.048	11	12489	1.115
5	12379	1.059	12	12346	1.130
6	12469	1.077	13	12367	1.141
7	12347	1.093	14	12389	1.184
HxCDD					
1	124679	1.000	6	123478	1.072
2	124689	1.000	7	123678	1.081
3	123468	1.009	8	123469	1.091
4	123679	1.040	9	123789	1.122
5	123689	1.040	10	123467	1.151

isomer an RRT on DB-5 greater than that of 2378-TCDF which is different from this report and ref. 15 and probably incorrect.

For the close eluting isomer pair 1349/1267-TCDF, Waddell *et al.* [35] reported an RRT on DB-5 slightly later than 2378-TCDF whereas all other work including this one find an RRT slightly earlier than 2378-TCDF on this non-polar phase. Whether this difference is due to variation in phase type, GC conditions or other factors is not certain. All of the above groups report the same RRT for these isomers on SP-2330.

Ligon and May [21] gave separations on Silar 10C, a 100% cyanopropyl phase similar to CP-Sil 88. Those shown for 1249- and 2468-TCDF, for 1269-TCDF (after 2378-TCDF), and 2346/2367-TCDF (reversed in ref. 21) all differ significantly from other work including the present one on the equivalent phase, CP-Sil 88. Separations reported by all groups for the other homologues of the PCDFs are the same for the two types of cyanopropyl columns. Whether the differences for the TCDFs are due to manufacturing processes or misidentification is not clear.

Recently, the US EPA [58] reported an isomer specific separation on a DB-225 phase of 2378-TCDF from all other TCDFs including the near elutors, 2347-TCDF

TABLE X

GC RETENTION TIMES OF PCDF/PCCD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A CPS-1 FUSED-SILICA CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000			
2	1378	1.086	20	1236	1.239
3	1379	1.086	21	2468	1.239
4	1347	1.097	22	1349	1.267
5	1468	1.111	23	1278	1.286
6	1247	1.111	24	1279	1.321
7	1367	1.124	25	1267	1.321
8	1348	1.139	26	1469	1.322
9	1346	1.157	27	1249	1.325
10	1248	1.157	28	2368	1.345
11	1246	1.174	29	2467	1.394
12	1237	1.188	30	1239	1.410
13	1268	1.188	31	2347	1.428
14	1369	1.188	32	1269	1.437
15	1478	1.188	33	2378	1.456
16	1234	1.220	34	2348	1.459
17	1678	1.220	35	2346	1.482
18	1238	1.239	36	2367	1.499
19	1467	1.239	37	3467	1.566
–	13468-PnCDF	1.316	38	1289	1.586
–	1368-TCDD	1.047	–	123468-HxCDF	1.719
PnCDF					
1	13468	1.000	15	12378	1.176
2	12468	1.014	16	12346	1.176
3	13678	1.055	17	12379	1.188
4	13479	1.065	18	12367	1.205
5	12368	1.085	19	12469	1.205
6	13478	1.085	20	12678	1.222
7	12478	1.099	21	12679	1.263
8	12479	1.109	22	12369	1.275
9	13467	1.118	23	23468	1.296
10	12467	1.130	24	12349	1.304
11	12347	1.134	25	12489	1.319
12	14678	1.144	26	23478	1.408
13	13469	1.159	27	12389	1.415
14	12348	1.171	28	23467	1.450
HxCDF					
1	123468	1.000	9	123678	1.103
2	134678	1.013	10	123467	1.119
3	134679	1.013	11	123679	1.131
4	124678	1.024	12	123469	1.183
5	124679	1.050	13	123689	1.183
6	123478	1.091	14	123789	1.295
7	123479	1.091	15	123489	1.332
8	124689	1.096	16	234678	1.399

TABLE X *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	2378	1.215
2	1379	1.054	13	1237	1.215
3	1378	1.109	14	1238	1.220
4	1369	1.132	15	1236	1.228
5	1247	1.140	16	1279	1.241
6	1248	1.140	17	1469	1.279
7	1268	1.171	18	1278	1.295
8	1478	1.192	19	1239	1.308
9	1246	1.204	20	1269	1.323
10	1234	1.211	21	1267	1.456
11	1249	1.215	22	1289	1.605
–	12468-PnCDD	1.379	–	124679-HxCDD	1.791
–	1368-TCDF	0.955			
PnCDD					
1	12468	1.000	8	12378	1.136
2	12479	1.000	9	12369	1.146
3	12368	1.031	10	12489	1.150
4	12478	1.058	11	12467	1.150
5	12379	1.080	12	12346	1.163
6	12469	1.104	13	12367	1.176
7	12347	1.113	14	12389	1.242
HxCDD					
1	123468	1.000	6	123478	1.075
2	124679	1.000	7	123678	1.085
3	124689	1.000	8	123469	1.110
4	123679	1.044	9	123789	1.148
5	123689	1.044	10	123467	1.175

(earlier) and 1239-TCDF (later). Both this work and that of Harden *et al.* [40] find the same elution order as above but the resolution between 2378-TCDF and 1239-TCDF is small. Again this difference may be affected by injection techniques, temperature programming or even slight variation in the phases themselves.

PnCDFs. The earliest complete collection of data for this homologue is that of Rappe [19] followed by Bell and Gara [22] both on the polar phase SP-2330. For the isomers, 13479- and 13478-PnCDF, the elution order given by Bell and Gara [22] is as written above while that of Rappe [19] is reversed. We agree with Bell and Gara [22] for both the SP-2330 and CP-Sil 88 phases *i.e.* 13479-PnCDF elutes before 13478-PnCDF and the latter co-elutes with 12368-PnCDF. Similarly, Bell and Gara [22] found that the isomer 12678-PnCDF (equivalent to 23489-) co-eluted with 12469-PnCDF followed much later by 23468-PnCDF. Rappe [19] has the elution order 23468- and 12678-PnCDF —we concur with the 1985 data [22]. The elution order given by Rappe [19] for the above pentafuran isomers has been used for structure assignment by Zoller and Ballschmiter [32] in chlorophenol pyrolysates, by Abraham *et al.* [59] in a rat study, by Wakimoto *et al.* [60] in determination of PCDFs in PCBs, and by Oehme *et*

TABLE XI

GC RETENTION TIMES OF PCDF/PCCD ISOMERS RELATIVE TO RT REPRENCE STANDARDS ON A SP-2331 FUSED-SILICA CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1467	1.330
2	1378	1.115	21	1236	1.330
3	1379	1.115	22	1349	1.371
4	1347	1.133	23	1278	1.383
5	1468	1.149	24	1267	1.435
6	1247	1.163	25	1279	1.435
7	1367	1.163	26	1469	1.457
8	1348	1.187	27	1249	1.461
9	1346	1.218	28	2368	1.473
10	1248	1.218	29	2467	1.533
11	1246	1.250	30	1239	1.576
12	1268	1.250	31	2347	1.582
13	1478	1.256	32	1269	1.616
14	1369	1.256	33	2378	1.633
15	1237	1.256	34	2348	1.639
16	1678	1.312	35	2346	1.667
17	1234	1.312	36	2367	1.685
18	2468	1.330	37	3467	1.770
19	1238	1.330	38	1289	1.835
–	13468-PnCDF	1.356	–	123468-HxCDF	1.845
–	1368-TCDF	1.062			
PnCDF					
1	13468	1.000	15	12378	1.240
2	12468	1.026	16	12346	1.249
3	13678	1.070	17	12379	1.262
4	13479	1.091	18	12367	1.277
5	12368	1.114	19	12469	1.300
6	13478	1.114	20	12678	1.300
7	12478	1.137	21	12679	1.368
8	12479	1.158	22	12369	1.389
9	13467	1.158	23	23468	1.405
10	12467	1.181	24	12349	1.432
11	14678	1.192	25	12489	1.453
12	12347	1.192	26	23478	1.546
13	13469	1.225	27	12389	1.569
14	12348	1.240	28	23467	1.593
HxCDF					
1	123468	1.000	9	124689	1.123
2	134678	1.009	10	123467	1.131
3	134679	1.012	11	123679	1.148
4	124678	1.026	12	123469	1.206
5	124679	1.064	13	123689	1.206
6	123478	1.105	14	123789	1.308
7	123479	1.105	15	123489	1.347
8	123678	1.114	16	234678	1.385

TABLE XI *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	1246	1.288
2	1379	1.068	13	1249	1.288
3	1378	1.137	14	1238	1.288
4	1369	1.180	15	1236	1.311
5	1247	1.182	16	1279	1.311
6	1248	1.182	17	1469	1.380
7	1268	1.220	18	1278	1.384
8	1478	1.252	19	1239	1.406
9	2378	1.266	20	1269	1.431
10	1237	1.281	21	1267	1.467
11	1234	1.288	22	1289	1.592
–	12468-PnCDD	1.430	–	124679-HxCDD	1.894
–	1368-TCDF	0.941			
PnCDD					
1	12468	1.000	8	12378	1.167
2	12479	1.000	9	12369	1.184
3	12368	1.037	10	12467	1.195
4	12478	1.076	11	12489	1.198
5	12379	1.098	12	12346	1.222
6	12469	1.146	13	12367	1.229
7	12347	1.146	14	12389	1.390
HxCDD					
1	123468	1.000	6	123478	1.069
2	124679	1.000	7	123678	1.077
3	124689	1.000	8	123469	1.111
4	123679	1.038	9	123789	1.130
5	123689	1.040	10	123467	1.162

al. [61] in PCDFs from magnesium smelting. Interestingly, Rappe *et al.* [62] correctly report the elution order of 12678-/23468-PnCDF in their more recent study on urban air.

HxCDFs. The only discrepancy we noted for the HxCDF homologues is for the 134678/124678-HxCDF pair which we and Bell and Gara [22] report as resolved peaks in the above order on the polar SP-2330 and CP-Sil 88 columns and not as first reported [19] in reverse order, and subsequently used to assign isomers in fly ash [60] and urban air [62].

2378-substituted PCDD/PCDF. Since the 2378-substituted PCDD/PCDF congeners are so important in both environmental and biological samples, their separation for the tetra-, penta- and hexa-homologues is shown in more detail in Tables XIV and XV for all nine GC phases. From Table XIV for the PCDDs, it is seen that the polar cyanopropyl columns such as SP-2331 and CP-Sil 88, and the smectic liquid crystalline phase can separate both 2378-TCDD from the other 21 isomers and the other four higher chlorinated 2378-substituted PCDDs from their respective isomers. The medium polar DB-17 is next best in the separation of these compounds with only

TABLE XII

GC RETENTION TIMES OF PCDF/PCCD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A CP-Sil 88 FUSED-SILICA CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1236	1.277
2	1378	1.095	21	2468	1.289
3	1379	1.095	22	1349	1.306
4	1347	1.111	23	1278	1.318
5	1468	1.125	24	1279	1.361
6	1247	1.135	25	1267	1.361
7	1367	1.135	26	1469	1.378
8	1348	1.156	27	1249	1.382
9	1346	1.182	28	2368	1.403
10	1248	1.183	29	2467	1.450
11	1268	1.208	30	1239	1.473
12	1246	1.208	31	2347	1.489
13	1237	1.216	32	1269	1.507
14	1478	1.216	33	2378	1.529
15	1369	1.218	34	2348	1.534
16	1678	1.258	35	2346	1.555
17	1234	1.258	36	2367	1.569
18	1238	1.277	37	3467	1.636
19	1467	1.277	38	1289	1.681
–	13468-PnCDF	1.291	–	123468-HxCDF	1.670
–	1368-TCDD	1.013			
PnCDF					
1	13468	1.000	15	12378	1.194
2	12468	1.022	16	12346	1.206
3	13678	1.055	17	12379	1.211
4	13479	1.073	18	12367	1.224
5	13478	1.093	19	12469	1.246
6	12368	1.093	20	12678	1.246
7	12478	1.112	21	12679	1.304
8	12479	1.129	22	12369	1.324
9	13467	1.129	23	23468	1.347
10	12467	1.147	24	12349	1.359
11	12347	1.153	25	12489	1.383
12	14678	1.158	26	23478	1.487
13	13469	1.185	27	12389	1.498
14	12348	1.194	28	23467	1.529
HxCDF					
1	123468	1.000	9	124689	1.128
2	134678	1.007	10	123467	1.132
3	134679	1.009	11	123679	1.150
4	124678	1.024	12	123469	1.224
5	124679	1.063	13	123689	1.224
6	123478	1.102	14	123789	1.349
7	123479	1.102	15	123489	1.403
8	123678	1.116	16	234678	1.471

TABLE XII *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	1246	1.249
2	1379	1.059	13	1249	1.249
3	1378	1.116	14	1238	1.249
4	1369	1.160	15	1236	1.269
5	1247	1.160	16	1279	1.269
6	1248	1.160	17	1278	1.327
7	1268	1.193	18	1469	1.339
8	1478	1.222	19	1239	1.350
9	2378	1.227	20	1269	1.376
10	1237	1.241	21	1267	1.403
11	1234	1.249	22	1289	1.509
–	12468-PnCDD	1.405	–	124679-HxCDD	1.818
–	1368-TCDF	0.987			
PnCDD					
1	12468	1.000	8	12378	1.133
2	12479	1.000	9	12369	1.153
3	12368	1.027	10	12467	1.162
4	12478	1.060	11	12489	1.167
5	12379	1.077	12	12346	1.185
6	12347	1.123	13	12367	1.191
7	12469	1.123	14	12389	1.265
HxCDD					
1	123468	1.000	6	123478	1.073
2	124679	1.000	7	123678	1.082
3	124689	1.000	8	123469	1.129
4	123679	1.042	9	123789	1.145
5	123689	1.042	10	123467	1.191

1469-TCDD interfering. The non-polar DB-1 and DB-5 columns have many congeners which co-elute with the 2378-substituted PCDDs.

In the case of the 2378-substiuted PCDFs (Table XV), the situation is more complicated. Only the DB-17 column was successful in our hands in separating 2378-TCDF from the other 37 TCDFs. The more polar DB-210, SP-2331 and CP-Sil 88 all had difficulty separating 2348-TCDF from 2378-TCDF. Interestingly, the other bonded phase methyl-phenyl (50%) (OV-17) column did not separate 1469- from 2378-TCDF. There may be major differences in the resolving power of this and other phases depending on batch number and manufacturer in addition to GC conditions such as temperature and injection mode. However the OV-17 column did allow complete isomeric identification of 12378-PnCDF which DB-17 did not (interference from 12346-PnCDF on the latter column). DB-210 was also successful in the separation of 12378- from 12348-PnCDF which the cyanopropyl and methyl silicone columns could not accomplish. The non-polar DB-1 and DB-5 have many isomers in the tetra- and penta-series which potentially overlap with the 2378-substituted PCDFs. As mentioned previously, the DB-225 column we used could not separate 1239-TCDF

TABLE XIII

GC RETENTION TIMES OF PCDF/PCDD ISOMERS RELATIVE TO RT REFERENCE STANDARDS ON A LIQUID CRYSTALLINE SMECTIC FUSED-SILICA CAPILLARY COLUMN

Reference standards as in Table V.

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDF					
1	1368	1.000	20	1236	1.331
2	1468	1.016	21	2368	1.331
3	1346	1.074	22	1378	1.389
4	2468	1.095	23	1379	1.430
5	1246	1.107	24	2346	1.450
6	1248	1.144	25	1238	1.470
7	1478	1.144	26	2467	1.483
8	1369	1.151	27	1269	1.490
9	1467	1.168	28	2348	1.508
10	1268	1.168	29	1278	1.508
11	1678	1.175	30	1239	1.624
12	1348	1.191	31	1267	1.624
13	1347	1.215	32	1279	1.646
14	1469	1.233	33	2347	1.737
15	1247	1.233	34	3467	1.764
16	1349	1.253	35	1237	1.786
17	1234	1.253	36	1289	1.822
18	1367	1.292	37	2378	1.865
19	1249	1.302	38	2367	1.865
–	13468-PnCDF	1.386	–	123468-HxCDF	2.077
–	1368-TCDD	1.095			
PnCDF					
1	13468	1.000	15	23468	1.311
2	12468	1.006	16	12348	1.333
3	14678	1.133	17	12678	1.384
4	13469	1.156	18	12369	1.404
5	13678	1.201	19	12349	1.444
6	12368	1.212	20	12347	1.464
7	12478	1.221	21	12679	1.507
8	13478	1.228	22	12489	1.522
9	12469	1.238	23	12367	1.583
10	13467	1.242	24	23478	1.589
11	13479	1.242	25	12378	1.664
12	12346	1.248	26	23467	1.712
13	12467	1.269	27	12379	1.742
14	12479	1.280	28	12389	1.962
HxCDF					
1	123468	1.000	9	123678	1.249
2	124678	1.020	10	123467	1.278
3	134678	1.020	11	123479	1.289
4	134679	1.046	12	123679	1.323
5	124679	1.079	13	234678	1.365
6	124689	1.113	14	123689	1.369
7	123469	1.163	15	123489	1.581
8	123478	1.233	16	123789	2.228

TABLE XIII *(continued)*

Elution order	Isomer	RRT	Elution order	Isomer	RRT
TCDD					
1	1368	1.000	12	1234	1.239
2	1369	1.042	13	1269	1.288
3	1478	1.100	14	1378	1.338
4	1246*[a]	1.140	15	1239	1.425
5	1249*	1.153	16	1279	1.472
6	1248*	1.179	17	1238	1.539
7	1469	1.188	18	1278	1.586
8	1379	1.199	19	1267	1.601
9	1268	1.199	20	1237	1.613
10	1236	1.199	21	1289	1.646
11	1247*	1.205	22	2378	1.915
–	12468-PnCDD	1.482	–	124679-HxCDD	2.098
–	1368-TCDF	0.913			
PnCDD					
1	12468*	1.000	8	12489*	1.231
2	12479*	1.032	9	12467*	1.250
3	12469	1.053	10	12347	1.279
4	12368	1.092	11	12367	1.318
5	12478	1.103	12	12379	1.343
6	12369	1.111	13	12378	1.478
7	12346	1.191	14	12389	1.577
HxCDD					
1	124679*	1.000	6	123689*	1.108
2	124689*	1.015	7	123478	1.202
3	123469	1.072	8	123678	1.207
4	123468	1.079	9	123467	1.360
5	123679*	1.096	10	123789	1.661

[a] Congeners marked with an asterisk are pairs which cannot be unequivocably assigned (*cf.* text).

from 2378-TCDF although this has been reported by others [58]. With regard to the HxCDFs, Table XV shows that a combination of using both a non-polar and medium or high polar column will allow unequivocal identification of all 2378-substituted HxCDFs and indeed of all 16 isomers.

The data show that all the isomers and congeners can be separated from each other by a combination of a minimum of two columns. In particular, all of the biologically important 2378-substituted PCDDs/PCDFs commonly found in animal species are readily differentiated on two GC columns. It is emphasized that, due to factors such as variation in columns and GC conditions, each laboratory must test the resolving power of their GC columns by demonstrating that those isomers eluting in the immediate vicinity of the congener in question as judged from this report are in fact suitably resolved. This information is the most comprehensive to date with regard to the number of single congeners reported and with respect to the number and range of polarity of the capillary columns. It also provides a confirmation of much earlier work. Except for six closely related PCDD pairs, the isomeric PCDD–PCDF content can be

TABLE XIV

ISOMERS WHICH COULD POTENTIALLY INTERFERE WITH THE 2378-SUBSTITUTED PCDDs ON FUSED-SILICA SILICONE CAPILLARY GC COLUMNS

Percent resolution between isomers in brackets; GC conditions as in Table IV.

2378-isomer	GC phase									
	DB-1	DB-5	DB-17	OV-17	DB-210	DB-225	CPS-1	SP-2331[a]	CP-Sil 88	Smectic
2378	1239 (50%)	1237 (50%) 1238 (30%)	1469 (0%)	1279 (0%)	1269 (0%)	1246 (0%) 1249 (30%)	1234 (0%) 1249 (0%) 1237 (0%) 1238 (40%)	1237 (100%; 0%)	1478 (50%)	None
12378	12367 (60%)	None	None	12346 (10%)	12367 (10%)	12369 (0%)	None	12369 (100%; 0%)	None	None
123478	123678 (60%)	123678 (50%)	None	None	None	None	None	None	None	123678 (20%)
123678	123478 (60%)	123478 (50%)	None	None	None	None	None	None	None	123478 (20%)
123789	123467 (0%)	123467 (0%)	None	None	None	None	None	None	None	None

[a] Resolution for SP-2331 in brackets shown first for a new column and then for one which has deteriorated with use.

TABLE XV

ISOMERS WHICH COULD POTENTIALLY INTERFERE WITH THE 2378-SUBSTITUTED PCDFs ON FUSED-SILICA SILICONE CAPILLARY GC COLUMNS

Percent resolution between isomers in brackets; GC conditions as in Table IV.

2378-isomer	GC phase									
	DB-1	DB-5	DB-17	OV-17	DB-210	DB-225	CPS-1	SP-2331[a]	CP-Sil 88	Smectic
2378	2347, 2348 1249, 1279, 2346 (all 0%)	2348, 2347, 2346, 1249, 1279 (all 0%)	None	1469 (0%)	2348 (70%)	1239 (10%)	2348 (10%)	2348 (30; 0%)	2348 (30%)	2367 (0%)
12378	12348 (90%)	12348 (10%)	12346 (0%)	None	12367 (0%) 12678 (0%)	13469 (10%)	12346 (0%)	12346 (100; 0%) 12348 (0; 100%)	12348 (0%)	None
23478	12679 (0%) 23467 (50%) 12369 (50%)	12489, 12679, 12369 (all 0%)	None	None	None	None	12389 (70%)	None	None	12367 (20%)
123478	123467 (10%)	123467 (0%)	124689 (50%)	None	123467 (0%) 123479 (10%) 123678 (70%)	None	123479 (0%) 124689 (10%)	123479 (0%; 0%)	123479 (0%)	None
123678	None	123479 (60%)	123467 (10%)	123467 (30%)	123467 (70%) 123479 (70%) 123478 (70%)	124689 (0%) 123479 (0%)	None	124689 (0;100%)	None	None
234678	123689 (0%)	123689 (90%)	123689 (70%)	123689 (50%)	None	123489 (0%)	None	None	None	123689 (0%)
123789	123489 (40%)	123489 (70%)	None	None	123489 (0%)	None	None	None	None	None

[a] Resolution for SP-2331 in brackets shown first for a new column and then for one which has deteriorated with use.

unambiguously specified for complex environmental samples containing many peaks or for the simpler biologically incurred samples containing mostly 2378-PCDD/PCDFs.

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