Journal of Chromatography, 107 (1975) 295–310

CHROM. 8143

ANALYSIS OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS IN CHLORINATED PHENOLS BY MASS FRAGMENTOGRAPHY

HANS-RUDOLF BUSER

Swiss Federal Research Station for Arboriculture, Viticulture and Horticulture, CH-8820 Wädenswil (Switzerland)

(Received November 11th, 1974)

SUMMARY

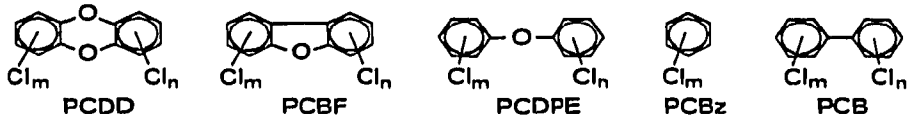
A rapid, highly specific method for the analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in pentachlorophenol and other chlorinated phenols is described. The rapid sample preparation procedure includes an alkaline extraction of phenolic compounds and chromatography of the neutral substances on an alumina micro-column. After gas chromatographic separation, individual polychlorinated dibenzo-*p*-dioxins and dibenzofurans are detected and quantified by mass fragmentography. The sample purification procedure removes polychlorinated diphenyl ethers, polychlorinated biphenyls and benzenes, phthalates and polychlorinated phenoxyphenols (predioxins), which might otherwise severely interfere in the analysis. Significant levels of hexa-, hepta- and octachlorodibenzo-*p*-dioxin and of hexa-, hepta- and octachlorodibenzofuran were found in two commercial products.

INTRODUCTION

Thousands of tons of pentachlorophenol (PCP) and other chlorinated phenols are used annually as herbicides, insecticides and wood preservatives. PCP is produced technically by chlorination of phenol or hydrolysis of hexachlorobenzene. Chlorinated phenols may contain a variety of by-products and contaminants, including other chlorophenols, polychlorinated phenoxyphenols (PCPPs), alkaline insoluble compounds such as polychlorinated diphenyl ethers (PCDPEs), polychlorinated dibenzofurans (PCBFs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated benzenes (PCBzs), polychlorinated biphenyls (PCBs) and some other minor constituents[1,2].

PCDDs and PCBFs have both been found to be extremely toxic, teratogenic and acnegenic compounds[3–5]. Heat treatment of chlorophenols or their alkali metal salts has been shown to produce significant amounts of PCDDs through a condensation process[6,7]. Elevated temperature and alkaline conditions are the most likely cause

STRUCTURES OF NEUTRAL COMPONENTS



STRUCTURES OF PHENOLIC COMPONENTS

for the formation of PCDDs and PCBFs during the synthesis of chlorophenols. These toxic materials can remain in the final products and therefore present a threat to life and the environment; the presence of PCDDs in fats used for preparing feeds has caused the deaths of millions of chickens (chick edema disease) and the treatment with PCP of hides used for preparing these fats was suggested as the probable source for this contamination[8].

As a safeguard against these dangerous chemicals, highly sensitive and specific analytical techniques are required in order to ensure that acceptable quality standards are maintained for chlorinated phenols. So far, gas chromatography with electron capture detection has mainly been used[1,9]. Owing to the presence of many other chlorinated components, the results are often questionable, and when extensive clean-up was used low recoveries were obtained. Mass spectrometry has been shown to be an extremely specific means for detecting selected PCDDs, *e.g.*, for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (tetra-CDD) in biological materials by time-averaged high-resolution mass spectrometry[10] and in technical 2,4,5-T herbicide formulations using quadrupole mass fragmentography[11]. Crummett and Stehl[12] used combined gas chromatography–mass spectrometry (GC–MS) for the analysis of series of PCDDs and PCBFs. They mentioned that PCDPEs may interfere in the determination of PCBFs. In other techniques, perchlorination of PCDDs[13] to octachlorodibenzo-*p*-dioxin (octa-CDD) or dechlorination to dibenzo-*p*-dioxin[14] was carried out, followed by analysis for these compounds. Whereas both methods may be excellent for obtaining the total amount of dioxins present, they do not permit the determination of the toxicologically very different individual compounds[3] within the group of PCDDs.

This paper describes a sensitive, highly specific method with a rapid sample preparation procedure for the analysis of PCDDs and PCBFs. The phenolic compounds in a sample are extracted with alkali and the neutral components are subjected to chromatography on an alumina micro-column so as to remove interfering components such as PCDPEs and possibly PCBs. After gas chromatographic separation, the individual PCDDs and PCBFs are detected and quantified by mass fragmentography. The application of the technique is demonstrated with the analysis of technical 2,3,4,6-tetrachlorophenol (TCP, Dowicide-6) and technical PCP (Dowicide-7). The method is currently in use for monitoring the levels of PCDDs and PCBFs in commercial samples.

EXPERIMENTAL

Instrumentation and operating conditions

A Finnigan Model 1015 D quadrupole mass spectrometer equipped with a venting system and a glass-jet separator to interface with the GC column was used. A glass column (2 m × 2 mm I.D.) was packed with 3% silicone OV-1 on Chromosorb W AW DMCS. The helium carrier gas flow-rate was adjusted to 25 ml/min. The column was operated under temperature-programmed conditions (140–260° at 10°/min) or isothermally at 260°. The injection port was maintained at 300° and the separator at 260°. Mass spectra were recorded with the electron impact source operated at 70 eV. The ion energy used was 8 V and the electron multiplier voltage was 3 kV. A scan time of 2 sec was found to be suitable for an *m/e* range of 35–620. Chromatograms were recorded using the total ion monitor (*m/e* 100–620).

For mass fragmentography, the instrument was operated at unit resolution and the ion source conditions were optimized for round-topped MS peaks and maximum sensitivity at *m/e* 414 (FC-43). The filter setting was reduced to 10 a.m.u./sec*. The precision mass meter was utilized for focusing specific ions at selected *m/e* values on to the detector. Daily calibration was carried out with perfluorotributylamine (FC-43) bleeding from a leak valve into the ion source, using the peaks at *m/e* 326, 376, 414, 426, 464 and 502. No multiple-ion monitoring equipment was available and therefore the results at different *m/e* values were obtained from individual injections.

Reagents and reference compounds

Light petroleum (b.p. 40–65°) and lithium hydroxide of purum quality and methanol and diethyl ether of puriss quality were obtained from Fluka (Buchs, Switzerland). Methylene chloride and ethyl acetate were of analytical grade and *n*-hexane was of pesticide quality (Merck, Darmstadt, G.F.R.). Aluminium oxide (basic, cationotropic) was used as received from Woelm (Eschwege, G.F.R.).

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (tetra-CDD) was obtained as a reference compound from Stickstoffwerke Linz (Linz, Austria). Hexachlorodibenzo-*p*-dioxin (hexa-CDD) was prepared by pyrolysis of potassium 2,3,4,6-tetrachlorophenate at 300°. The sublimate was purified by multiple recrystallization from toluene. A hexa-CDD purity of at least 90% was indicated by MS, GC and micro-elemental analysis. Octachlorodibenzo-*p*-dioxin (octa-CDD) and octachlorodibenzofuran (octa-CBF) were commercially available from Analabs (North Haven, Conn., U.S.A.). Solutions of these standards were prepared in ethyl acetate or *n*-hexane at concentrations ranging from 1 to 100 ng/μl. The safety precautions to be taken when preparing and handling these highly toxic materials have been stressed elsewhere[15].

Sample preparation and analysis

PCP (Dowicide-7) and TCP (Dowicide-6) were initially analyzed by MS using the direct insertion probe and by GC–MS after methylation of the samples. Methyl ether derivatives were prepared by reacting *ca.* 100 mg of each phenol in 10%

* a.m.u. = Atomic mass units.

methanol–diethyl ether with an excess of diazomethane. After dilution, *ca.* 5–10 μg of the derivatives were injected in the GC–MS.

For analysis of the neutral components, phenolic compounds were removed from the samples by an alkaline extraction. Four grams of PCP or TCP were dissolved in 30 ml of methanol; 10 ml of 2.5 *N* lithium hydroxide solution and 100 ml of distilled water were then added. Extraction was carried out by vigorous shaking with 40 ml of light petroleum. After separation, the aqueous phase was checked for alkalinity (pH > 12) and drained off. In case the separation was incomplete or difficult to achieve, 2–5 g of anhydrous sodium sulphate were added in order to break the emulsion. The organic phase that remained in the separating funnel was washed with 100 ml of distilled water containing 2 ml of 2.5 *N* lithium hydroxide solution followed by a second wash with 50 ml of distilled water. The pH value of the last washing should be neutral. After drying the organic phase over anhydrous sodium sulphate, a 20-ml aliquot corresponding to 2 g of phenol was carefully concentrated to about 2 ml in a stream of nitrogen. Some samples may form a yellowish solution and a sediment consisting mainly of octa-CDD.

The neutral components were further purified by chromatography on an alumina micro-column. Into a 15-cm disposable Pasteur pipette (15 cm × 5 mm I.D.) containing a small plug of glass-wool, 1.0 g of dry aluminium oxide was added and the column packed tightly by tapping. The concentrate containing the neutral components was carefully added to the column by pipette. Any precipitates were transferred quantitatively on to the column using small portions of freshly prepared 2% methylene chloride in *n*-hexane. The column was then eluted using a total of 10 ml of this eluent. This first fraction was shown to contain PCBzs and PCDPEs. Any PCBs present in samples will also be eluted with this solvent. A second fraction containing PCDDs and PCBFs was taken by elution with 10 ml of 50% methylene chloride in *n*-hexane. Completeness of elution of these components was checked by taking a third fraction with 10 ml of 100% methylene chloride. The micro-column was packed so as to approximate to a flow-rate of 1 drop every 1–2 sec with the first eluent.

For GC–MS analysis of the components present, 0.5-ml aliquots of these fractions were carefully concentrated 5–10 times, 10 μl injected (corresponding to 10–20 mg of original phenol) under temperature-programmed conditions and chromatograms (total ion monitor) and mass spectra recorded. For comparison, chromatograms of the concentrates containing the neutral components prior to alumina chromatography were obtained.

Mass fragmentographic analyses at selected *m/e* values were carried out isothermally at 260° by injecting 10 μl-aliquots (corresponding to 2 mg of original phenol) of the alumina fractions. In case a sample should contain individual PCDDs above the 1000 ppm level, smaller samples of phenol may be required for extraction because saturation of the light petroleum by PCDDs may otherwise occur.

RESULTS AND DISCUSSION

Direct analysis of the chlorinated phenols

Two commercial chlorinated phenols, PCP (Dowicide-7) and TCP (Dowicide-6), were analyzed by mass spectrometry using the direct insertion probe. In PCP ($M^+ = 264$), the mass spectra showed the presence of some tetrachlorophenol

($M^+ = 230$) as impurity. At elevated probe temperatures (180–220°), the presence of compounds of higher molecular weight was indicated. A cluster of peaks at *m/e* 492–504 (Cl_9) suggests the presence of a significant amount of nonachlorophenoxyphenol (nona-CPP, $M^+ = 492$), as reported previously by Rappe and Nilsson[16]. Clusters at *m/e* 456–468 found in this spectrum are probably due to some octa-CDD ($M^+ = 456$) and octa-CPP ($M^+ = 458$) present in this sample. In TCP, direct-probe MS showed the presence of PCP. At higher probe temperatures (200°), chlorine clusters were observed at *m/e* 458 to 468 (Cl_8) and at *m/e* 424 to 432 (Cl_7), indicating the presence of octa-CPP ($M^+ = 458$) and hepta-CPP ($M^+ = 424$). A Cl_6 cluster at *m/e* 388–396 may be due to $M^+ - HCl$ from hepta-CPP rather than from hexa-CDD. These results indicate the presence of dimeric compounds in both samples.

The samples were further investigated by GC–MS analysis following methylation. Fig. 1 shows chromatograms of PCP and TCP analyzed as their methyl ether derivatives on a temperature-programmed OV-1 column using the total ion monitor (TIM). The peaks observed were identified by MS, as indicated on the chromatograms. The chromatograms show the presence of 1% of TCP (TIM, peak area) in PCP and 15% of PCP in TCP. In both samples, several peaks at longer retention times were observed. The mass spectra of these peaks were consistent with those reported for the methyl ether derivatives of PCPPs[16,17]. In PCP, the presence of 3% of nona-CPP (TIM, methyl ether derivative, $M^+ = 506$, Cl_9 cluster) and some octa-CPP ($M^+ = 472$, Cl_8 cluster) was indicated. The mass spectra showed molecular ions (M^+) with fragmentation leading to clusters at $M^+ - 15$ (CH_3), $M^+ - 35$ (Cl, weak), $M^+ - 50$ (CH_3Cl), $M^+ - 70$ (Cl_2), $M^+ - 85$ and $M^+ - 113$. The changing intensities of these peaks, mainly $M^+ - 15$, $M^+ - 50$ and $M^+ - 70$, suggests the presence of several isomers in each instance. In TCP, about 4% of hepta-CPP (TIM, methyl ether derivative, $M^+ = 438$, Cl_7 cluster) and some octa-CPP was found. These levels of PCPPs are within the range reported[2].

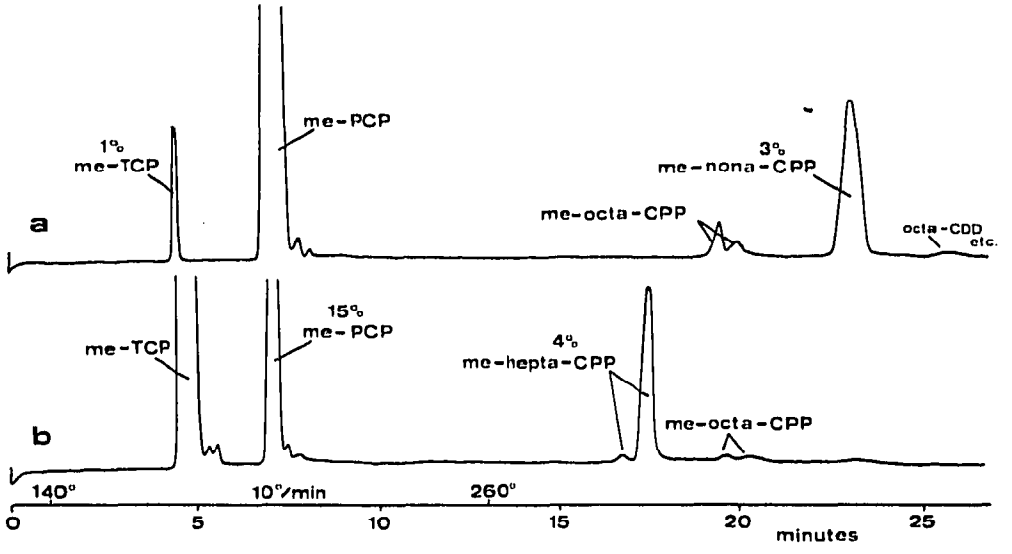


Fig. 1. Chromatograms of methylated chlorophenols (OV-1, 140–260° at 10°/min, total ion monitor), me = methyl ether derivatives. (a) PCP (Dowicide-7); (b) TCP (Dowicide-6).

Analysis of neutral components in alumina fractions by GC–MS

In our analysis, most of the phenolic compounds in a sample were removed by alkaline extraction, and separation of the neutral components was then achieved on an alumina adsorption micro-column. After experimenting with different adsorbents and elution solvents, the system described was found to be the most efficient for a rapid clean-up. A similar micro-column system has been described for the separation of PCBs from some PCDDs[18]. We have adopted this system by changing the volumes and concentrations so that any PCBs, in addition to PCDPEs, are removed from PCBFs and PCDDs. In the mass fragmentographic analysis, the presence of PCDPEs would severely interfere with PCBFs. Basic alumina as adsorbent was selected in order to improve the retention capacity for phenolic compounds. A third fraction was taken initially to check the completeness of elution of PCDDs and PCBFs in fraction II. For routine analysis of PCDDs and PCBFs, fraction III would not be required and fraction I can be discarded. Fraction III has been found to contain any phthalates that may be present, although their recovery may not be complete owing to hydrolysis during sample preparation. A scheme of analysis is presented in Fig. 2.

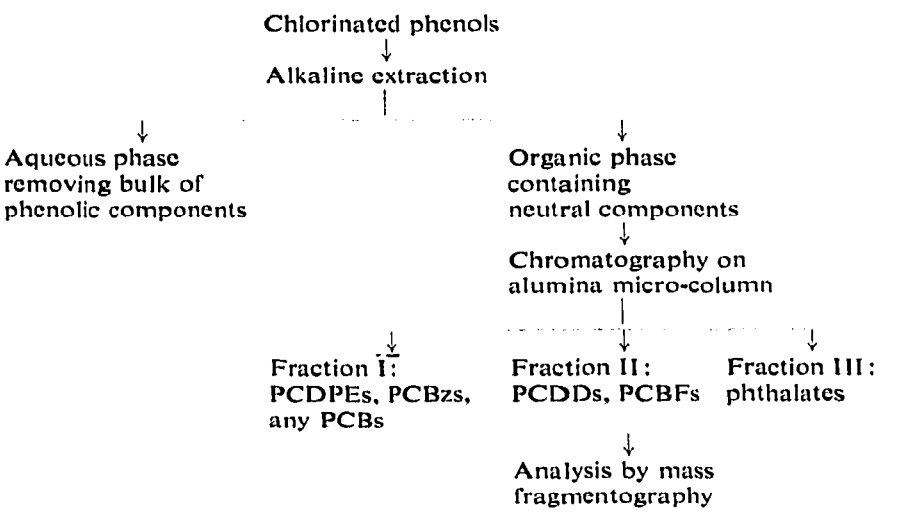


Fig. 2. Analysis scheme for chlorinated phenols.

Each group of compounds such as PCDDs, PCBFs or PCDPEs consists of a multitude of individual members containing up to 8–10 chlorine atoms in isomeric positions. Silicone OV-1 was chosen for GC because this stationary phase is expected to give the least selectivity towards isomers, but sufficient separating power for compounds of a group that differ in the number of chlorine atoms present. This grouping effect was desired as at this stage we were not interested in individual isomers. In addition, this stationary phase showed excellent high-temperature stability. The alumina fractions of the neutral components were injected under temperature-programmed conditions. Chromatograms of these fractions are given in Fig. 3 for PCP and in Fig. 4 for TCP. Those obtained for the neutral components prior to alumina chromatography corresponded to the sum of the individual chromatograms.

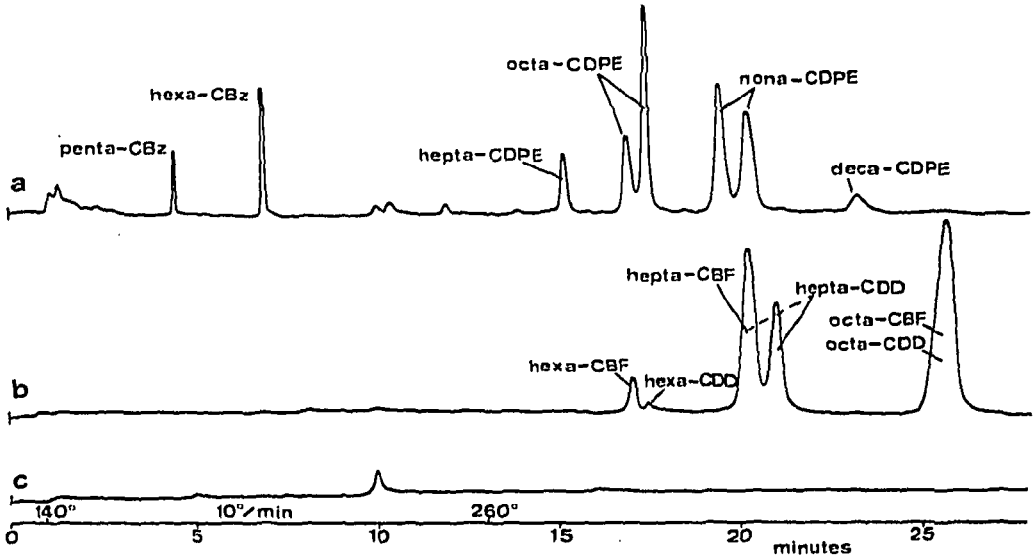


Fig. 3. Chromatograms of neutral components in PCP (Dowicide-7). OV-1, 140–260° at 10°/min, total ion monitor. (a), Fraction I; (b), fraction II; (c), fraction III.

Most components in these fractions could readily be identified from their mass spectra by the presence of their molecular ions, the number of chlorine atoms indicated by the ion clusters and their fragmentation patterns. Alumina fraction I of PCP contained penta- and hexa-chlorobenzene (penta- and hexa-CBz), hepta-, octa-, nona- and deca-chlorodiphenyl ether (hepta- to deca-CDPE) and some

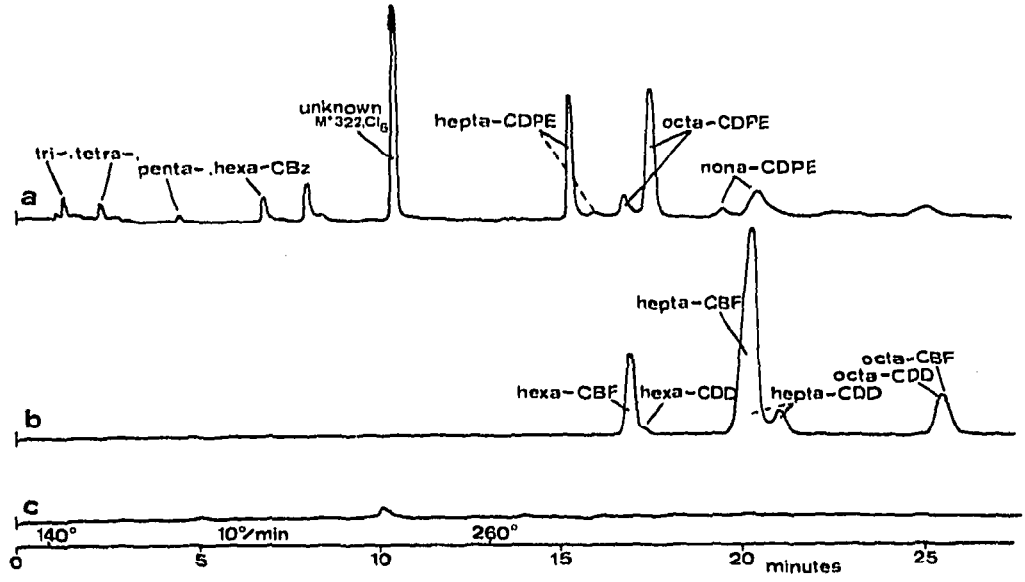


Fig. 4. Chromatograms of neutral components in TCP (Dowicide-6). OV-1, 140–260° at 10°/min, total ion monitor. (a), fraction I; (b), Fraction II; (c), fraction III.

minor unknown compounds; the corresponding fraction of TCP contained tri-, tetra-, penta- and hexa-CBz, hepta-, octa- and nona-CDPE and one major and some minor unknown compounds. Alumina fraction II of PCP and TCP contained hexa-, hepta- and octa-CDD and hexa-, hepta- and octa-CBF. Alumina fraction III contained trace amounts of some phthalates; their source was not investigated further.

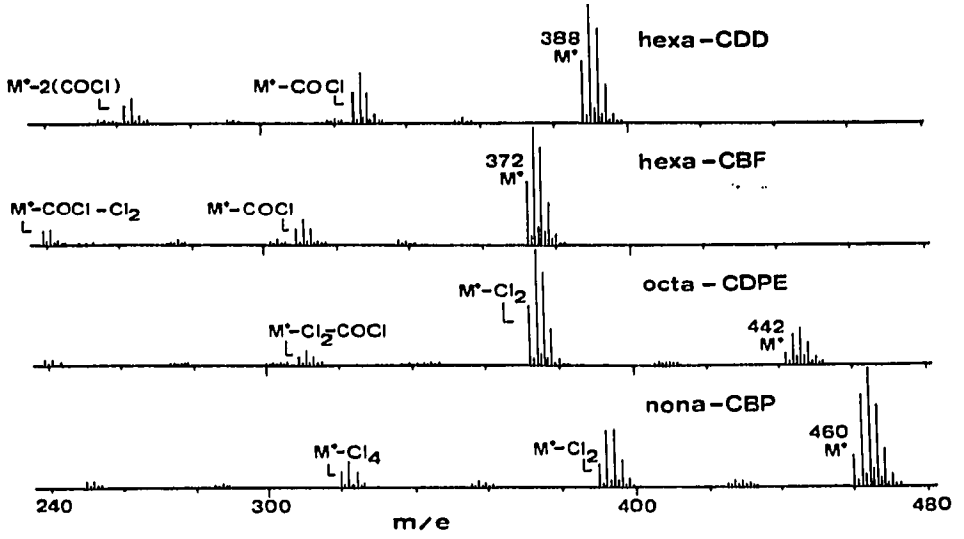


Fig. 5. Mass spectra (*m/e* 240–480) of hexa-CDD, hexa-CBF, octa-CDPE and nona-CBP.

Fig. 5 shows mass spectra of hexa-CDD, hexa-CBF, octa-CDPE and nonachlorbiphenyl (nona-CBP). These compounds are eluted at about the same GC retention time and their mass spectra are representative of individual groups. In Table I the mass spectra for individual components of each group are given. For simplicity, only the first ion in each chlorine cluster is listed and the lower mass ranges are neglected. Table I contains only the higher chlorinated members of each group. The ion clustering observed was as expected from the natural abundance of the chlorine isotopes. Spectra for PCBs are included for reference; these compounds may be present as additional contaminants. In Fig. 6 the fragmentation patterns of PCDDs, PCBFs, PCDPEs and PCBs are shown. The fragmentation of PCDPEs leads to ions ($M^+ - Cl_2$, base peak) with the same exact mass and number of chlorine atoms as a corresponding PCBF (Table I). Mixtures of these compounds are difficult to analyze without prior separation on the alumina column because they are eluted with similar GC retention times. Lowering ionization energy to 18 eV did not overcome this situation: the $M^+ - Cl_2$ ion was still a major ion formed with PCDPEs. In addition, at low electron energies, the $M^+ - COCl$ ions in PCDDs and PCBFs are depressed, which is undesirable as these ions are characteristic and diagnostic features of these compounds.

Mass fragmentographic analysis of alumina fractions

The separation of neutral components on the alumina micro-column was

TABLE I

MASS SPECTRAL CHARACTERISTICS OF PCDDs, PCBFs, PCDPEs AND PCBs

Only the first ion in each chlorine cluster and in the higher mass range is listed.

Compound	*Ion and m/e*						
PCDD	M^+ *(v. strong)*	$M^+ - Cl$ *(weak)*	$M^+ - COCl$ *(strong)*	$M^+ - Cl_2$ *(weak)*	$M^+ - CO - Cl_2$ *(weak)*	$M^+ - 2COCl$ *(medium)*	M^{2+} *(medium)*
Tetra	320	285	257	250	222	194	160
Penta	354	319	291	284	256	228	177
Hexa	388	353	325	318	290	262	194
Hepta	422	387	359	352	324	296	211
Octa	456	421	393	386	358	330	228
PCBF	M^+ *(v. strong)*	$M^+ - Cl$ *(weak)*	$M^+ - COCl$ *(strong)*	$M^+ - Cl_2$ *(weak)*	$M^+ - CO - Cl_2$ *(weak)*	$M^+ - COCl - Cl_2$ *(medium)*	M^{2+} *(medium)*
Tetra	304	269	241	234	206	171	152
Penta	338	303	275	268	240	205	169
Hexa	372	337	309	302	274	239	186
Hepta	406	371	343	336	308	273	203
Octa	440	405	377	370	342	307	220
PCDPE	M^+ *(strong)*	$M^+ - Cl$ *(weak)*	$M^+ - HCl$ *(weak)*	$M^+ - Cl_2$ *(v. strong)*	$M^+ - Cl_3$ *(weak)*	$M^+ - Cl_2 - COCl$ *(medium)*	$M^+ - Cl_4$ *(weak)*
Hexa	374	339	338	304	269	241	234
Hepta	408	373	372	338	303	275	268
Octa	442	407	406	372	337	309	302
Nona	476	441	440	406	371	343	336
Deca	510	475	—	440	405	377	370
PCB	M^+ *(v. strong)*	$M^+ - Cl$ *(weak,med.)*	$M^+ - HCl$ *(weak)*	$M^+ - Cl_2$ *(strong)*	$M^+ - Cl_3$ *(weak)*	$M^+ - HCl - Cl_2$ *(weak)*	$M^+ - Cl_4$ *(medium)*
Hexa	358	323	322	288	253	252	218
Hepta	392	357	356	322	287	286	252
Octa	426	391	390	356	321	320	286
Nona	460	425	424	390	355	354	320
Deca	494	459	—	424	389	—	354

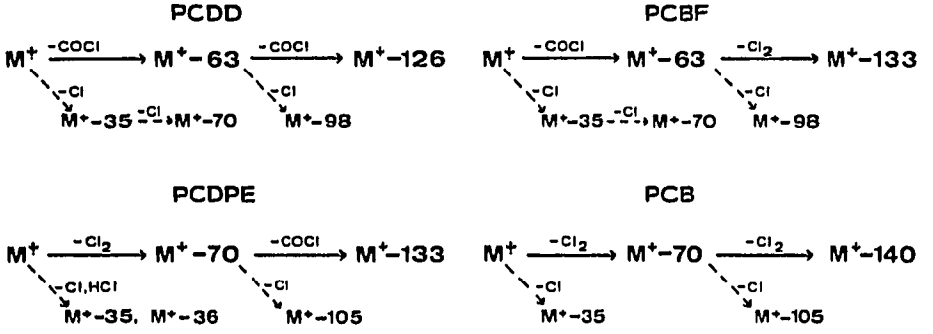


Fig. 6. Fragmentation of PCDDs, PCBFs, PCDPEs and PCBs leading to ions in higher mass range.

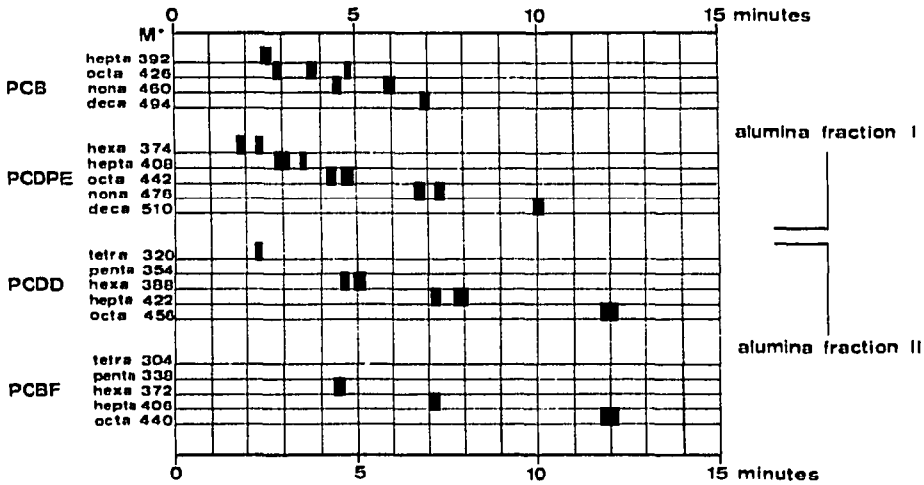


Fig. 7. Retention times of PCBs, PCDPEs, PCDDs and PCBFs on OV-1 at 260°.

further investigated by mass fragmentographic analysis in order to check the presence or absence of individual components in each alumina fraction. Re-analysis of standards and alumina fractions of PCP and TCP was carried out isothermally at 260° to determine retention times under these conditions. These retention times are reported graphically in Fig. 7. The *m/e* values used to monitor individual components were

TABLE II

RESULTS SHOWING ELUTION OF PCDPEs AND PCBs IN ALUMINA FRACTION I

Compound	*Ion (m/e)*	*Sample*	*Content (% rel.)**	
			Fraction I	*Fraction II*
Hexa-CDPE	304 $M^+ - Cl_2$	TCP	100 (3)	$\leq$0.5
		PCP	100 (3)	$\leq$1
Hepta-CDPE	408 M^+	TCP	100 (1)	$\leq$0.1
		PCP	100 (1)	$\leq$0.2
Octa-CDPE	442 M^+	TCP	100 (2)	$\leq$0.5
		PCP	100 (2)	$\leq$0.4
Nona-CDPE	478 $M^+ + 2$	TCP	Low level	—
		PCP	100 (2)	$\leq$0.4
Deca-CDPE	442 $M^+ + 2 - Cl_2$	TCP	Not found	–
		PCP	100 (1)	$\leq$0.4
Octa-CBP	426 M^+	Aroclor 1268 (100 µg)	100 (2)	$\leq$0.1
Nona-CBP	460 M^+	Aroclor 1268 (100 µg)	100 (2)	$\leq$0.1
Deca-CBP	426 $M^+ + 2 - Cl_2$	Aroclor 1268 (100 µg)	100 (1)	$\leq$0.5
Hexa-CBz**	284 $M^+ + 2$	Standard (12 µg)	100 (1)	$\leq$0.05

* Number of isomers observed indicated in parentheses; results of alumina fractions III not included ($<$0.05%).

** Hexa-CBz analyzed at 180°.

selected from Table I. In Table II, results obtained for monitoring PCDPEs and PCBs are given. The results are reported as a percentage of the total amount and are based on comparisons of peak height measurements. They indicate that all PCDPEs (hexa- to deca-CDPE) are contained completely ($> 99.5\%$) in alumina fraction I. The same was found with PCBs and hexa-CBz. Fraction I of PCP and TCP were checked for the presence of PCBs and hexa-CBz. Octa-, nona- and deca-CBP were below 0.5 ppm relative to Aroclor 1268, in which these components are the main constituents. The amounts of hexa-CBz present in both PCP and TCP were determined mass fragmentographically (*m/e* 284, $M^+ + 2$); levels of 100 and 20 ppm, respectively, were found.

The results reported in Table III for PCDDs and PCBFs indicate that these compounds are recovered to an extent of $> 96\%$ in alumina fraction II. Fractions III did not contain measurable concentrations of either component. In Figs. 8 and 9, the separation of PCDPEs and PCBFs on the alumina micro-column is demonstrated with two chromatograms; the results are included in Tables II and III.

Removal of polychlorinated phenoxyphenols (PCPPs) by the clean-up scheme

Polychlorinated phenoxyphenols (PCPPs), as the major by-products of chlori-

TABLE III

RESULTS SHOWING ELUTION OF PCDDs AND PCBFs IN ALUMINA FRACTION II

Compound	*Ion (m/e)*	*Sample*	*Content (% rel.)**	
			Fraction I	*Fraction II*
Tetra-CDD	320 M^+	TCP, PCP	—	Not found
		Standard (10 μg)	< 0.05	100 (1)
Penta-CDD	354 M^+	TCP, PCP	—	Not found
Hexa-CDD	388 M^+	TCP	Interference	—
		PCP	< 5	> 95 (3)
		Standard (10 μg)	< 0.05	100 (2)
		Isomers** (100 μg)	< 0.05	100 (3)
Hepta-CDD	422 M^+	TCP	< 10	> 90 (1)
		PCP	< 1.5	> 98 (2)
Octa-CDD	456 M^+	TCP	< 4	> 96 (1)
		PCP	< 0.5	100 (1)
		Standard (4 μg)	< 0.05	100 (10)
Tetra-CBF	304 M^+	TCP, PCP	—	Not found
Penta-CBF	338 M^+	TCP, PCP	—	Not found
Hexa-CBF	TIM	TCP	< 5–10	> 90–95 (1)
	372 M^+	PCP	Interference***	—
Hepta-CBF	406 M^+	TCP	< 2	> 98 (1)
	408 $M^+ + 2$	PCP	Interference***	—
Octa-CBF	440 M^+	TCP	< 0.2	100 (1)
		PCP	< 1.5	98 (1)
		Standard (10 μg)	< 0.05	100 (1)

* Number of isomers observed indicated in parentheses; results of alumina fractions III not included ($< 0.5\%$).

** Hexa-CDDs in raw product from pyrolysis of potassium 2,3,4,6-tetrachloro-, 2,4,5-trichloro- and pentachlorophenate.

*** Interferences due to the presence of octa- and nona-CDPE.

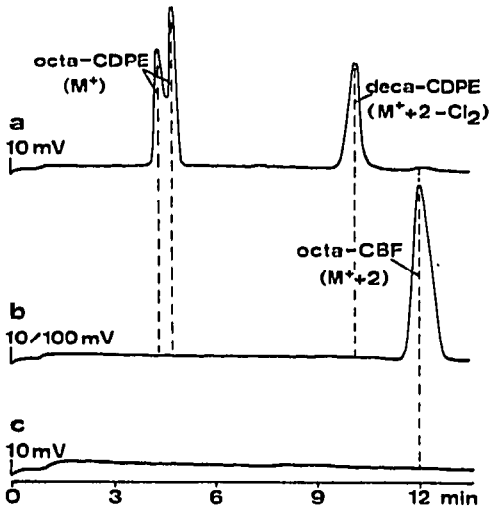
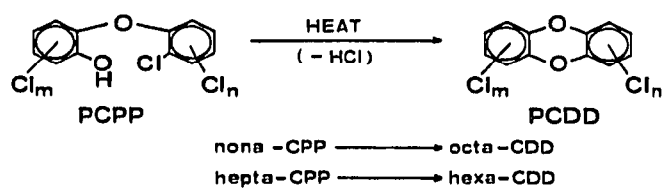


Fig. 8. Mass fragmentograms (*m/e* 442) of PCP (Dowicide-7). (a), Fraction I; (b), fraction II; (c), fraction III.

nated phenols, exist as several isomers of which the *ortho*-isomers are important as precursors of PCDDs (predioxins)[17]. It has been found that PCPPs can undergo ring closure by elimination of HCl upon injection into a gas chromatograph with the formation of a PCDD[19]:



PCPPs also give rise to an $M^+ - HCl$ ion with the same exact mass as a corresponding PCDD and could therefore interfere in the mass fragmentographic analysis.

For the accurate analysis of PCDDs, the complete removal of PCPPs must therefore be ensured. These compounds may escape removal by the alkaline extraction because of some steric hindrance of the phenolic hydroxyl group. Crummet and Stehl[12] have shown that with their ion-exchange clean-up, nona-CPP is removed at a level of 200 ppm; the levels actually encountered in samples in this study were 100 times greater. The removal of these compounds by our alkaline extraction and alumina chromatography therefore had to be investigated.

Alumina fractions II of PCP and TCP containing PCBFs and PCDDs were split in two equal parts (1-g aliquots): one half was methylated and analyzed for the presence of PCPPs directly, while the other half was fortified with 10 μg of the original PCP or TCP (standard solutions in methanol), then methylated and analyzed. A comparison of the peak heights of hepta-CPP obtained by mass fragmentographic analysis (methyl ether derivative, $M^+ = 438$, retention time 4.6 min) in the original

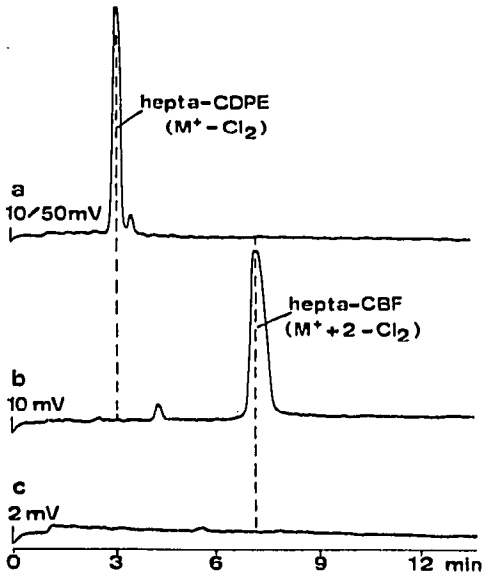


Fig. 9. Mass fragmentograms (*m/e* 338) of TCP (Dowicide-6). (a), Fraction I; (b), fraction II; (c), fraction III.

and the fortified TCP fractions indicated an amount in the former corresponding to that contained in 3 μg of original TCP. Similarly, the amount of nona-CPP (methyl ether derivative, $M^+ = 506$, retention time 9.8 min) in the non-fortified fraction was determined to correspond to the amount contained in 12 μg of original PCP. These values represent maximum levels as the peaks observed may actually be due to some interference. Because the level of PCPPs in commercial chlorinated phenols is expected to be in the 1–5% range, the final concentration in Fraction II will be about 0.1 ppm and therefore will not interfere in our PCDD analysis.

Analysis of PCDDs and PCBFs by mass fragmentography

PCDDs and PCBFs were determined in PCP and TCP by analyzing alumina fractions II using mass fragmentography. These fractions have been shown to contain mainly these two groups of compounds. Although individuals in each group are not completely separated from corresponding members of the other group by the GC column, the difference of 16 a.m.u. between the molecular ions of PCDDs and the corresponding PCBFs (Table I) nevertheless allows their specific detection by mass fragmentography. The difference of 16 a.m.u. is well out of the 8–12 a.m.u. ion cluster range (1% level) observed with compounds that contain 6–8 chlorine atoms.

Because our instrument was not equipped with a multiple-ion monitoring attachment, separate injections were required in order to analyze for all desired components. This time requirement will be drastically reduced when such equipment is available. Quantitation was achieved by comparing the peak heights for the samples with those of known amounts of standards. If such standards were not available, semi-quantitation was carried out by estimating the specific responses from interpolation of the response of available standards; the response for hepta-

TABLE IV

MASS FRAGMENTOGRAPHIC RESPONSE OF PCDD AND PCBF STANDARDS

Compound	*m/e*	*Amount injected (ng)*	*Area found* (mm²)***	*Specific response* (mm² mV ng⁻¹)*
Tetra-CDD	320	24	108 (20)	90
Hexa-CDD	388	20	288 (5)	72
Octa-CDD	456	100	615 (10)	62
Octa-CBF	440	100	620 (10)	62

* Chart speed, 1 cm/min; recorder, 250 mm full scale; pre-amplification, 10^{-7} A/V; specific response, 1 mm²·mV corresponding to $2.4 \cdot 10^{-12}$ Coulomb.

** Values in parentheses: mV.

CDD was estimated as the average of the responses of hexa- and octa-CDD, and that of penta-CDD as the average of the responses of tetra- and hexa-CDD. Octa-CDD and octa-CBF gave similar response values and it was assumed that the same would be true for other pairs of PCDDs and PCBFs. Response values have to be determined under identical conditions; they depend on the ion source and resolution adjustments. Typical values obtained are reported in Table IV.

Mass fragmentograms for both samples, PCP and TCP, are presented in Figs. 10 and 11 and the quantitative results are summarized in Table V. When multiple peaks were observed (hexa-CDD and hepta-CDD), a summation of the peaks was made and the total was reported irrespective of the isomers. Higher PCDDs and PCBFs may give responses at lower *m/e* values owing to the presence of fragment ions (*e.g.*, $M^+ - Cl_2$). The results in Table V indicate significant levels of hexa-, hepta- and octa-CDD and hexa-, hepta- and octa-CBF in both samples, whereas none of the tetra- and penta-analogues were found (retention time ranges for penta-CDD and tetra- and penta-CBF were estimated from the data in Fig. 7). The presence of the above compounds was established previously by mass spectrometry. The detection limit of about 0.2 ppm under the present conditions can be

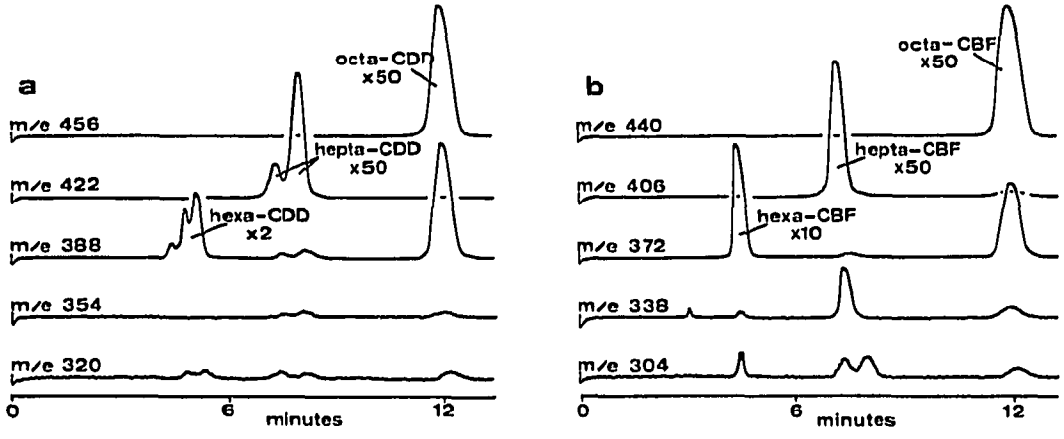


Fig. 10. Mass fragmentograms of PCP (Dowicide-7, alumina fraction II). (a), Determination of PCDDs; (b), determination of PCBFs. Sensitivity 1 mV or as indicated; OV-1, 260°.

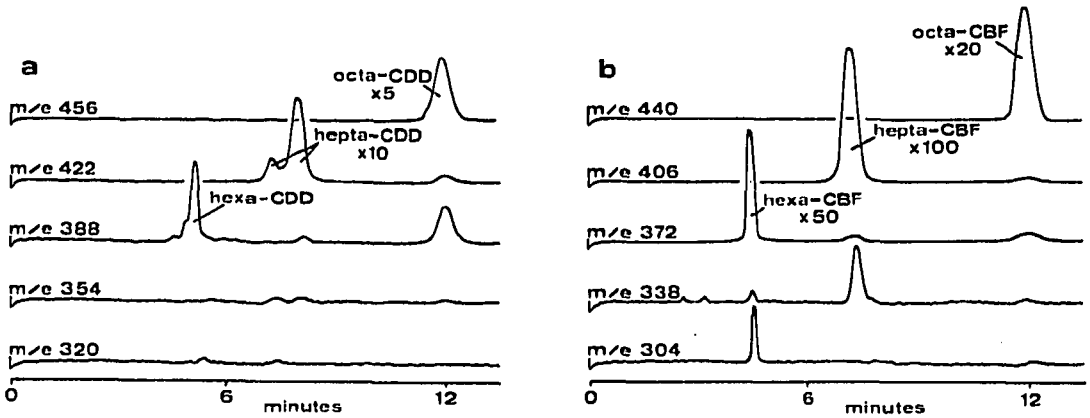


Fig. 11. Mass fragmentograms of TCP (Dowicide-6, alumina fraction II). (a), Determination of PCDDs; (b), determination of PCBFs. Sensitivity 1 mV or as indicated; OV-1, 260°.

TABLE V

CONTENT OF PCDDs AND PCBFs IN TWO COMMERCIAL CHLORINATED PHENOLS

Compound	*m/e*	*Content (ppm)*	
		TCP (Dowicide-6)	*PCP (Dowicide-7)*
Tetra-CDD	320	< 0.2	< 0.2
Penta-CDD	354	< 0.2	< 0.2
Hexa-CDD	388	6	9
Hepta-CDD	422	55	235
Octa-CDD	456	39	250
Tetra-CBF	304	< 0.2	< 0.2
Penta-CBF	338	< 0.2	< 0.2
Hexa-CBF	372	230	39
Hepta-CBF	406	500	280
Octa-CBF	440	135	230

decreased further by concentration of the alumina fractions and injection of larger aliquots; a decrease of at least 20-fold seems feasible (< 0.01 ppm). Recoveries were determined with hexa-CDD; the values ranged from 85% at the 0.2-μg level (0.05 ppm) to over 95% at the 10-μg level (2.5 ppm). Similar values were obtained with tetra-CDD and we expect that other PCDDs and PCBFs behave in a similar manner.

CONCLUSIONS

The method described, involving alkaline extraction to remove phenolic compounds, chromatography of the neutral components on an alumina micro-column and mass fragmentographic detection, proved to be a rapid means of analysis of commercial chlorinated phenols for the presence of highly toxic PCDDs and PCBFs. PCBzs, PCDPEs, PCBs and PCPPs (predioxins) were removed by the clean-up procedure. The removal of PCDPEs is important for an accurate analysis because these compounds yield mass spectrometric peaks at the same exact mass as PCBFs,

and the absence of PCPPs must be ensured as these compounds can be converted into PCDDs during GC. Two commercial products, Dowicide-6 and Dowicide-7, have been shown to contain significant levels of PCDDs and PCBFs.

ACKNOWLEDGEMENT

I thank Dr. H.-P. Bosshardt for helpful discussions during the course of this investigation and for comments on the manuscript.

REFERENCES

1 D. Firestone, J. Ress, N. L. Brown, R. P. Barron and J. N. Damico, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 85.
2 C. A. Nilsson and L. Renberg, *J. Chromatogr.*, 89 (1974) 325.
3 B. A. Schwetz, J. M. Norris, G. L. Sparschu, V. K. Rowe, P. J. Gehring, J. L. Emerson and C. G. Gerbig, in E. H. Blair (Editor), *Chlorodioxins —Origin and Fate*, American Chemical Society, Washington, D.C., 1973, Ch. 7, p. 55.
4 G. L. Sparschu, F. L. Dunn and V. K. Rowe, *Food Cosmet. Toxicol.*, 9 (1971) 405.
5 J. G. Vos, J. H. Koeman, H. L. van der Maas, M. C. ten Noever de Brauw and R. H. de Vos, *Food Cosmet. Toxicol.*, 8 (1970) 625.
6 H. G. Langer, T. P. Brady, L. A. Dalton, T. W. Shannon and P. R. Briggs, in E. H. Blair (Editor), *Chlorodioxins —Origin and Fate*, American Chemical Society, Washington, D.C., 1973, Ch. 4, p. 26.
7 H. G. Langer, T. P. Brady and P. R. Briggs, *Environ. Health Perspect.*, 5 (1973) 3.
8 L. D. Metcalfe, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 542.
9 E. A. Woolson, R. F. Thomas and P. D. J. Ensor, *J. Agr. Food Chem.*, 20 (1972) 351.
10 R. Baughman and M. Meselson, *Environ. Health Perspect.*, 5 (1973) 27.
11 H.-R. Buser and H.-P. Bosshardt, *J. Chromatogr.*, 90 (1974) 71.
12 W. B. Crummet and R. H. Stehl, *Environ. Health Perspect.*, 5 (1973) 15.
13 D. T. Williams and B. J. Blanchfield, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 93.
14 B. Zimmerli, *J. Chromatogr.*, 88 (1974) 65.
15 O. Aniline, in E. H. Blair (Editor), *Chlorodioxins —Origin and Fate*, American Chemical Society, Washington, D.C., 1973, Ch. 14, p. 126.
16 C. Rappe and C. A. Nilsson, *J. Chromatogr.*, 67 (1972) 247.
17 S. Jensen and L. Renberg, *Ambio*, 1 (1972) 62.
18 M. L. Porter and J. A. Burke, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 1426.
19 S. Jensen and L. Renberg, *Environ. Health Perspect.*, 5 (1973) 37.