CHLORINATED DIBENZOFURANS AND DIBENZO-P-DIOXINS: DETECTION AND QUANTITATION IN ELECTRICAL EQUIPMENT AND THEIR FORMATION DURING THE INCINERATION OF PCBs

by

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ABSTRACT

In this research, the formation of chlorinated dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs) in PCB based fluids was investigated. The amount of PCDFs in transformer askarels was found to depend upon the length of time the transformer (and askarel) had been in service. PCDFs were also found to form when PCB based fluids were exposed to high temperatures (ca 500°C) with oxygen present. No significant amounts of PCDDs were detected in either study.

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October, 1979

Mr. D. Pascoe,
Environmental Protection Service,
Department of Fisheries and
Environment,
135 St. Clair Ave. West,
2nd Floor,
Toronto, Ontario

Dear Mr. Pascoe,

Please find enclosed the final draft of the report entitled "Chlorinated Dibenzofurans and Dibenzo-p-dioxins: Detection and Quantitation in Electrical Equipment and Their Formation During the Incineration of PCBs" prepared for the Department of Fisheries and the Environment under contract number: OSS78-00067. We hope you find it satisfactory.

Yours very truly,

Brock Chittim — Steve Clegg

B.G. Chittim — B.S. Clegg

BGC/BSC/dec
Enclosure

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CONCLUSIONS

1. Significant levels of 2,3,7,8-tetrachlorodibenzofuran (TCDF) (i.e. ranging from ca. 0.005 to 5.0 ppm) were found in used transformer grade askarels.

2. The amount of chlorinated dioxins (PCDDs), if detected, was usually less than 5% of the TCDF concentration. It appears from these initial results that the PCDD levels in PCB based fluids are insignificant relative to even individual PCDF concentration.

3. Small amounts of terphenyls, quaterphenyls and chlorinated terphenyls were detected in some of the askarel samples but they were not quantified.

4. The amounts of TCDF in transformer askarels were found to increase as the time since the transformer was installed increased. Time-in-service was the only variable that could be positively attributed to the formation of PCDFs.

5. Although only a limited number of samples were available, the effects of discharging or arcing in a transformer on the levels of TCDF in the 'contained' askarel appears to be negligible. These periods of abnormal operation are most likely too short to cause the necessary reactions.

6. Laboratory scale pyrolysis of the PCB-based fluids at 500°C resulted in the formation of large amounts of PCDFs. No PCDDs were formed.

7. In this survey the askarel samples were only analyzed for TCDF since it has been shown to be the most toxic (extremely) of all of the PCDF congeners. It should also be pointed out that the analyses were carried out using 'packed' chromatographic columns and it is therefore possible that the peak corresponding to TCDF may be due to more than one PCDF congener.

RECOMMENDATIONS

1. During the sampling portion of this project it was noted that some units were poorly maintained (eg. corroded, leaking) and spill preventative measures had not been taken. It is suggested that a nation-wide inspection of all PCB-filled transformers be initiated. The purpose of this survey would be to locate units that are in need of maintenance or spill prevention equipment, and to instruct the owners of such units on what measures should be taken.

2. Due to the presence of PCDFs in transformer oils, particularly in the used askarels, the 'total' destruction of PCB based fluids that are no longer in use is even more imperative. In this respect, the method to be used for this destruction should be tested for:

   i) its potential to cause the formation of PCDFs from PCBs

   ii) its destruction efficiency with respect to PCDFs.

3. Recently it was found that PCDFs and, to a lesser extent, PCDDs, were formed by pyrolysis of chlorobenzenes in sealed quartz ampoules.[82] Since askarels are a mixture of chlorobenzenes and PCBs and it has been indicated that chlorobenzenes may be used for retrofilling askarel filled transformers, the formation of PCDFs from chlorobenzenes and the contamination of chlorobenzenes by PCDFs should be investigated.

4. Due to recent technical advances it is highly recommended that capillary gas chromatograph methods be developed for the analysis of environmental contaminants. Capillary chromatography would be especially applicable to analysis for PCBs, PCDFs and PCDDs where individual congeners have been shown to have distinct toxicological properties.

INTRODUCTION

The chlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have been detected as contaminants in a number of commercial products such as pentachlorophenol and PCBs. A number of individual PCDD and PCDF congeners have been found to be some of the most toxic compounds known to man. These compounds have also been detected as contaminants in various environmental samples.

In this report:

1) The chemical, physical and spectral properties of the known PCDD and PCDF isomers are briefly discussed.

2) The biological and toxicological properties of these two groups of chemicals are summarized and compared.

3) The literature concerning the prescence and formation of PCDF and PCDD in various commercial products, with emphasis on PCB-based fluids, reviewed and discussed.

4) Samples of askerals were taken from transformers which were operated under varying conditions in such a manner so that an operation or construction variable could be isolated. These samples were then analyzed for PCDDs and PCDFs.

5) Samples of PCBs and askerals were subjected to high temperatures (such as those which might be expected during a transformer fire) and the formation of PCDDs and PCDFs investigated.

The initial terms of reference for this project are given in Appendix B.

1 POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS: THEIR CHEMISTRY, BIOLOGICAL PROPERTIES AND FORMATION

The chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), as shown in Figure 1, have been found as highly stable contaminants in some widely used industrial chemicals. Their detection as environmental pollutants poses a threat to human health due to their lipophilic and extraordinary toxic nature.

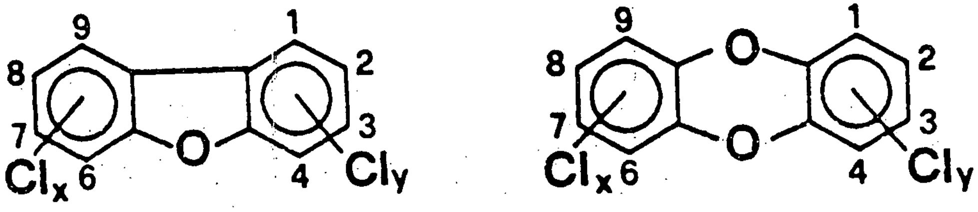


Figure 1: Chlorinated Dibenzofurans and Dibenzo-p-dioxins

1.1 CHEMICAL AND PHYSICAL PROPERTIES

1.1.1. Synthesis

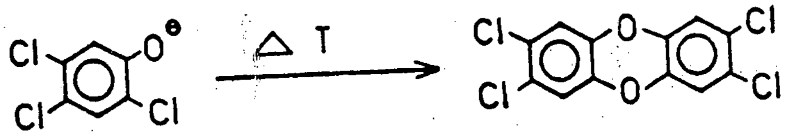
A total of 75 different PCDD isomers and 135 different PCDF isomers and congeners are possible (see Table 1); since each of these compounds have

TABLE 1: Number of positional PCDD and PCDF isomers

Chlorine substitution	Number of chlorines in each carbon ring x	y	PCDDs Number of isomers: in each sub-group	total	PCDFs Number of isomers: in each sub-group	total
mono -	1	0	2	2	4	4
di -	2	0	4		6	
	1	1	6	10	10	16
tri -	3	0	2		4	
	2	1	12	14	24	28
tetra -	4	0	1		1	
	3	1	8		16	
	2	2	13	22	21	38
penta -	4	1	2		4	
	3	2	12	14	24	28
hexa -	4	2	4		6	
	3	3	6	10	10	16
hepta -	4	3	2	2	4	4
octa -	4	4	1	1	1	1
				75		135

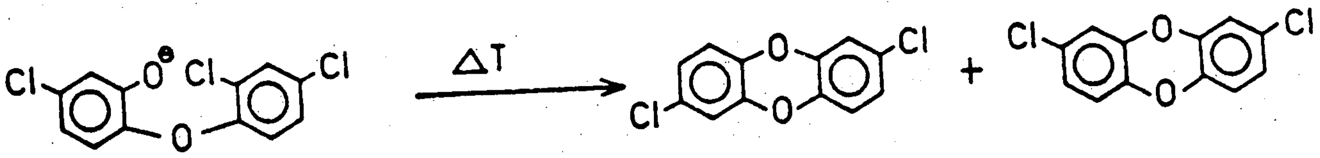
different toxicological properties, their individual synthesis and identification in mixtures is extremely important. Only a small number of papers have been published dealing with the synthesis of individual PCDD [1,2,3] and PCDF [4,5] compounds. The most common preparative routes for the PCDDs have been summarized by Buser.[6] They are:

- the dimerization of chlorophenates (1)[7],



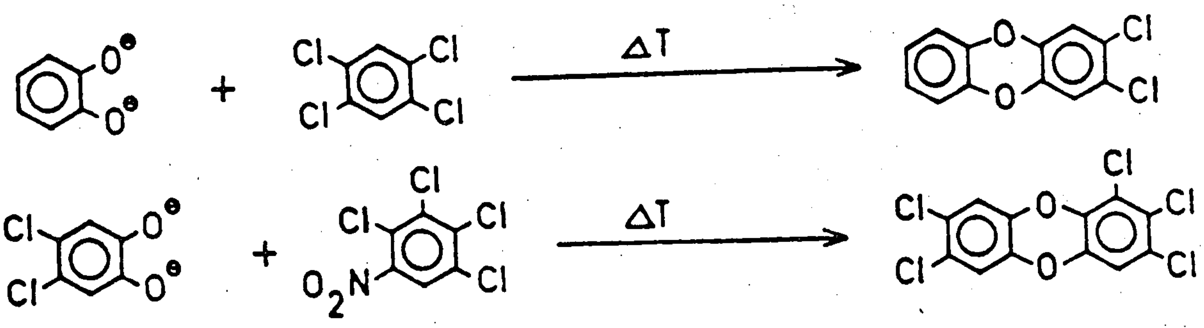
(1)

- the cyclization of chlorinated 2-phenoxyphenols (2)[8],



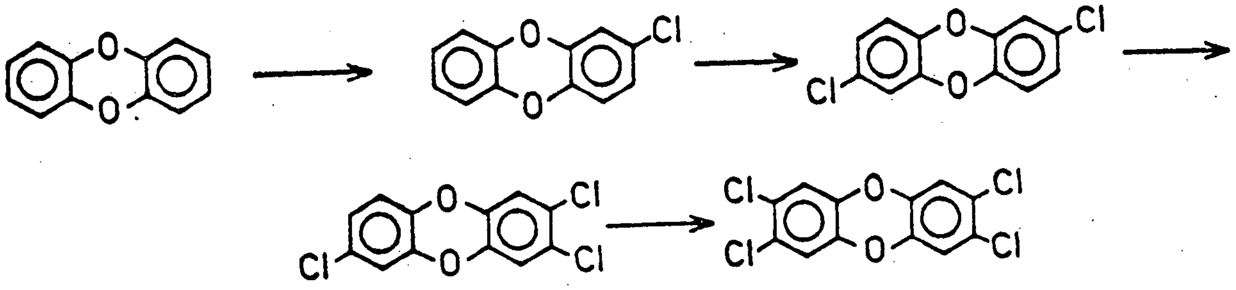
(2)

- the condensation of catechols with chlorobenzenes[1] or chloronitrobenzenes (3)[1,2],



(3)

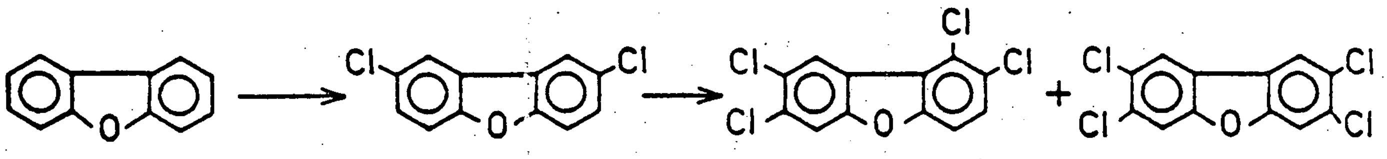
and the direct chlorination of dibenzo-p-dioxin (4).



(4)

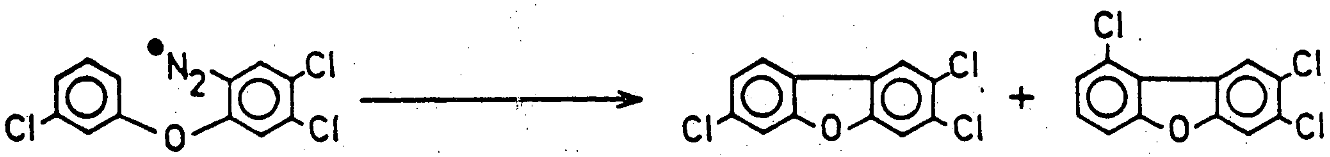
The major routes possible for the preparation of the various PCDF isomers have been investigated by Grey and his coworkers.[4] They are:

the direct chlorination of dibenzofuran(5),



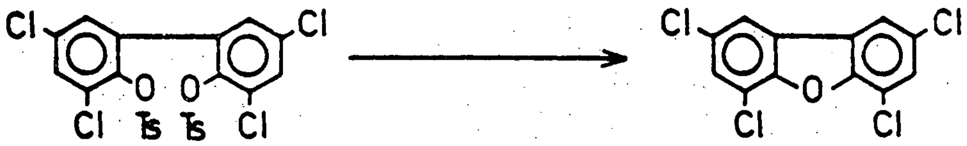
(5)

the diazotization and cyclization of substituted o-phenoxy anilines (6),



(6)

and, cyclization of substituted o,o'-biphenyols or their derivatives (7).



(7)

More recently, the synthesis of PCDFs has been achieved by the palladium catalyzed ring-closure[9], and by the photolysis[10] of some chlorinated diphenyl ethers.

1.1.2 General Properties

The individual PCDD and PCDF congeners are colourless solids at room temperature. The melting points of a few representative congeners are given in Table 2. Like the PCBs, the PCDDs and PCDFs are extremely insoluble in water and are only sparingly soluble in most organic solvents. At standard temperature and pressure they have no appreciable vapour pressure.

Table 2: Melting Points of some PCDD and PCDF Isomers

Dibenzo-*p*-dioxin	M.P. °C	Dibenzofuran	M.P. °C
unsubstituted	122-123	unsubstituted	86-87
1-chloro-	104.5-105.5	2-Chloro-	101.5
2-Chloro-	88-89	2,3-Dichloro-	125.5-127
2,7-Dichloro-	209-210	2,3,8-Trichloro-	189-191
2,8-Dichloro-	150.5-151	2,4,6-Trichloro-	116-117
2,3-Dichloro-	163-164	2,3,7,8-Tetrachloro-	227-228
1,2,4-Trichloro-	128-129	2,3,6,8-Tetrachloro-	202-203
2,3,7-Trichloro-	162-163	2,4,6,8-Tetrachloro-	198-200
1,2,3,4-Tetrachloro-	189	1,2,4,7,8-Pentachloro-	234-235
2,3,7,8-Tetrachloro-	320-325	Octachloro	256-257
1,3,6,8-Tetrachloro-	219-220		
1,2,3,4,7-Pentachloro-	195-196		
1,2,3,7,8-Pentachloro-	240-241		
1,2,4,7,8-Pentachloro-	205-206		
1,2,3,4,7,8-Hexachloro-	275		
1,2,4,6,7,9-Hexachloro-	238-240		
Octachloro	330-331		

1.1.3 Spectral Properties

The INFRARED SPECTRA (IR) of the PCDDs and the PCDFs show a characteristically strong band due to the stretching of the C-O-C bond[1,4,8]. The location of this absorption band varies with the position and number of the chlorine substituents[1]. The PCDD and PCDFs also exhibit bands due to the bending of the aromatic C-H bonds. When the hydrogens involved are isolated (the absence of any ortho substituted H-H interactions) the band occurs between 870 and 880 cm^{-1}. When these C-H bonds are adjacent the band occurs between 850 and 860 cm^{-1}.

The IR spectrum of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is shown in Figure 2 with the main bands characterized. Many of the PCDD and PCDF isomers can be distinguished from each other using their IR spectra.

The ULTRAVIOLET SPECTRAL (UV) data for a series of chlorinated dibenzo-*p*-dioxins and dibenzofurans is summarized in Table 3. The UV spectrum of dioxin

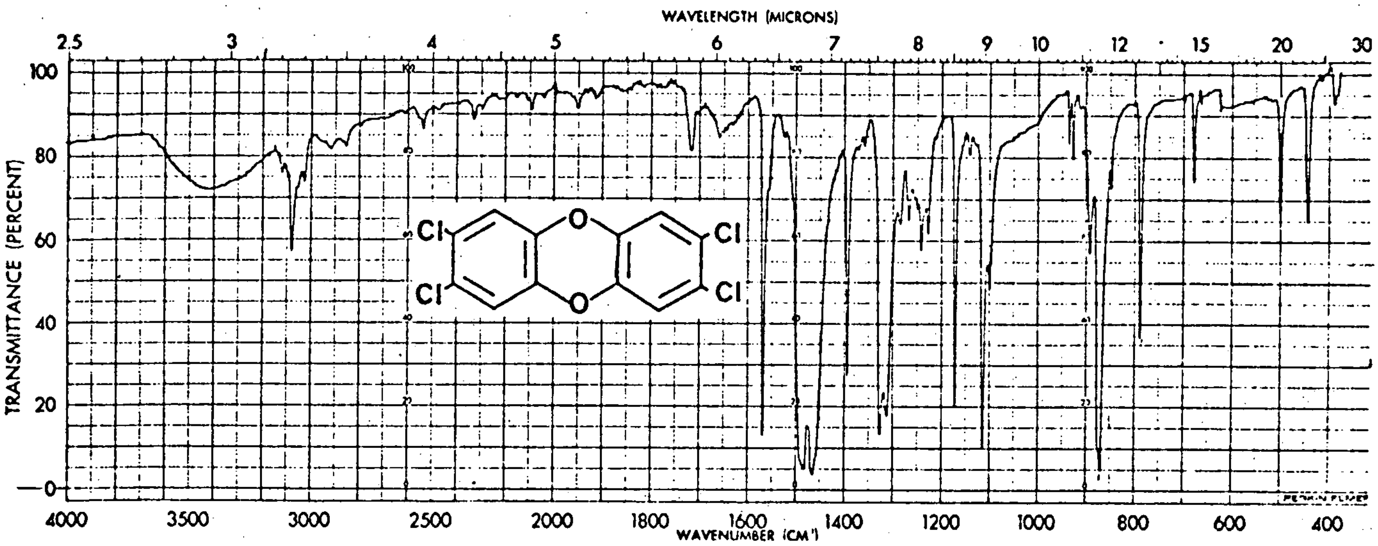


Figure 2.

Infrared spectrum of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Aromatic CH stretch: 3122 (uw), 3080(wm), 3028(w). C═C skeletal in-plane stretch: 1569(s), 1493(s sh), 1473(vs), 1464(vs), 1457(s sh), 1394(m). ═COC═ asymmetric stretch: 1327(s), 1212(s), CCC trigonal aromatic ring in-plane deformation 1173(s). Aromatic ring breathing 115(s). CH out-of-plane deformation 876(s sh), 870(vs). Aromatic CCl stretch 789(m)

in chloroform exhibits two maxima at 248 and 293; that of dibenzofuran is much more complex (see Table 3). The maxima of both compounds are shifted to higher wavelengths when chlorines are added to the aromatic ring.

The electron-impact (EI) MASS SPECTRA of the PCDDs and PCDFs both exhibit intense molecular ions (M^+) with the expected ion clustering due to the chlorine isotopes. Doubly-charged molecular ions (M^{2+}) of some intensity are also observed.[17] PCDDs mainly fragment to form M^+-COCl and M^+-2COCl ions [6,11], although minor fragmentation occurs by loss of Cl, Cl_2 and sometimes HCl from the molecular and fragment ions. A typical PCDD mass spectrum (EI), that of 2,3,7,8-tetrachlorodibenzo-p-dioxin, is shown in Figure 3.

Table 3: UV Spectral Data for some PCDD and PCDF Isomers

Dibenzo-p-dioxin	UV Spectral Data; $CHCl_3$ λmax (ε) (nm)
Unsubstituted	248(1020),293(3680)
1-chloro-	248(1320),294(3190)
2-chloro-	248(1140),299(3700)
2,7-dichloro-	247(1340),302(4590)
2,8-dichloro-	247(1180),299(4690)
2,3-dichloro-	247(1830),304(3190)
1,2,4-trichloro-	253(5290),294(2250)
1,2,3,4-tetrachloro-	257(6290),317(2290)
2,3,7,8-tetrachloro-	248(2970),310(5590)
1,3,6,8-tetrachloro-	250(5540),305(3440)
1,2,3,4,7-pentachloro-	259(5920),306(2690)
1,2,3,4,7,8-hexachloro-	259(5370),316(3660)
1,2,4,6,7,9-hexachloro-	259(4450),310(1480)
octachloro	261(13150),318(2400)
Dibenzofuran	
Unsubstituted	245(10000),250(20000),280(16000), 285(16000),295(10000),300(16000)
2,3,8-trichloro-	256(33000),302(29000),313(21000)
2,3,7,8-tetrachloro-	259(15000),306(15000),316(14000)
2,3,6,8-tetrachloro-	250(43000),260(52500),285(27400), 302(32000),314(14100)
2,4,6,8-tetrachloro-	257(17000),294(18600),310(5800), 323(5800)
1,2,4,7,8-pentachloro-	256(27000),266(41000),297(48000)
1,3,4,7,8-pentachloro-	263(27000),272(40000),297(48000), 320(18000)

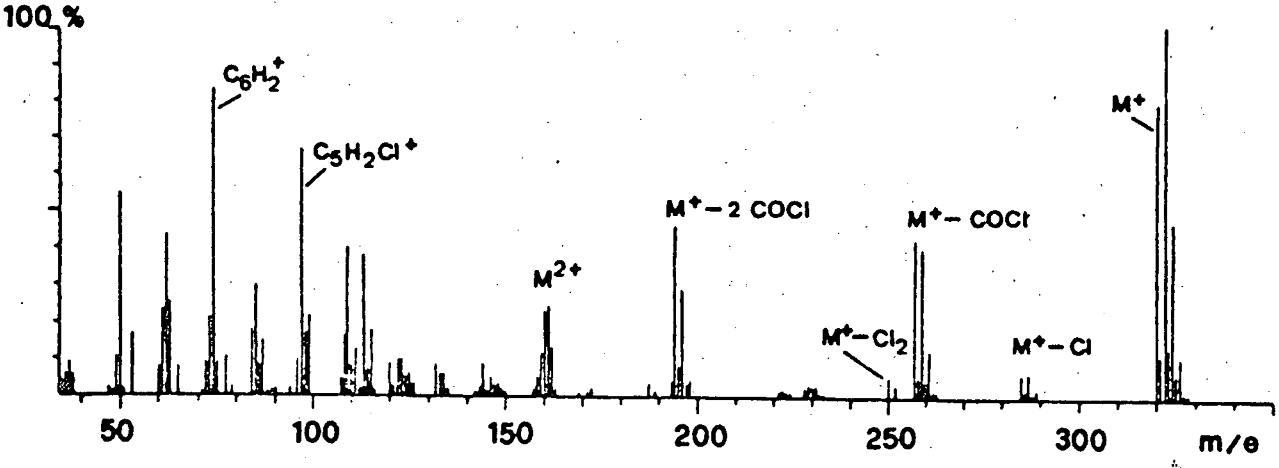


Figure 3 EI Mass Spectrum of 2,3,7,8-Tetrachlorodibenzo-p-dioxin

The PCDFs also show a typical fragmentation with M^+-COCl (M^+-63) and M^+-COCl-Cl_2(M^+-133) ions being formed. As with the PCDDs there is some minor fragmentation due to loss of Cl, Cl_2 and HCl. The EI mass spectrum (MS) of 2,3,7,8-tetrachlorodibenzofuran is shown in Figure 4.

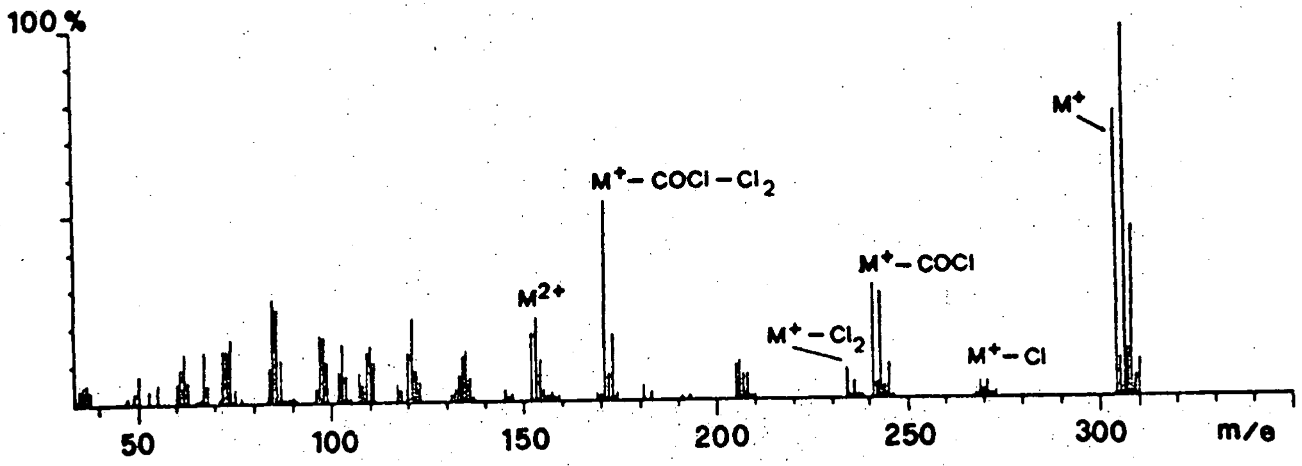


Figure 4.
EI Mass Spectrum of 2,3,7,8-Tetrachlorodibenzofuran

In most cases the molecular ions of the PCDDs and PCDFs easily distinguish them from other chlorinated aromatic hydrocarbons such as PCBs. There are, however, some compounds which potentially could interfer in MS analysis. For example, the identification of PCDFs may be complicated by the presence of chlorinated diphenylethers. These compounds yield intense ions (M^+-Cl_2) with the same exact mass and chlorine number as a corresponding PCDF. In this case, and in most others, such interfering compounds have different chromatographic properties and thus can be removed.[12]

NUCLEAR MAGNETIC RESONANCE (NMR) spectra, like IR, can be used to distinguish between various PCDD and PCDF isomers. NMR data for some of these compounds, synthesized by unambiguous methods, has previously been reported[1,2,4] and is summarized in Table 4.

Table 4: NMR Data for Representative PCDD and PCDF Isomers

Dibenzo-p-dioxin	Peak Pattern or Type and Number of Protons[a]	Actual Protons Involved[b] and Chemical Shift (ppm)[c]
Unsubstituted	AA'BB',8	6.81
1-chloro-	ABCD,4	} centred at 6.85
	ABC,3	
2-chloro-	AA'BB',4	6.78
	ABC,3	6.81
2,7-dichloro-	ABC,6	6.82
2,8-dichloro-	ABC,6	6.80
2,3-dichloro-	AA'BB',4	6.96
	s,2	H_1 and H_4 ; 7.02
1,2,4-trichloro-	m,4	H_{6-9} ; 6.88
	s,1	H_3 ; 7.00
2,3,7-trichloro-	m,3	H_6,H_8,H_9 ; 6.85
	s,2	H_1 and H_4 ; 6.97
2,3,7,8-tetrachloro-	s,4	H_1,H_4,H_6,H_9 ; 6.97
1,3,6,8-tetrachloro-	AB,4	6.90 and 7.02
1,2,3,4-tetrachloro-	m,4	H_{6-9} ; 6.96
1,2,3,4,7-pentachloro-	ABC,3	H_6,H_8,H_9 ; 6.96
1,2,3,7,8-pentachloro-	s,1	H_6 ; 6.98
	s,1	H_9 ; 7.02
	s,1	H_4 ; 7.13
1,2,4,7,8-pentachloro-	s,2	H_6 and H_9 ; 7.16
	s,1	H_3 ; 7.19
1,2,3,4,7,8-hexachloro-	s,2	H_6 and H_9 ; 6.96
1,2,3,6,7,9-hexachloro-	s,2	H_4 and H_8 ; 7.18
Dibenzofuran		
Unsubstituted	m,6	H_{2-4}, H_{6-8} ; 7.03-7.62
	m,2	H_1 and H_9 ; 7.82
2,3,8-trichloro-	d,2	H_6 and H_7 ; 7.48
	s,1	H_4 ; 7.68
	t,1	H_9 ; 7.84
	s,1	H_1 ; 7.95
2,3,9-trichloro-	m,3	H_6,H_7 and H_8 ; 7.25-7.8
	s,1	H_4 ; 7.85
	s,1	H_1 ; 8.5
2,4,6-trichloro-	m,2	H_7 and H_8 ; 7.36
	d,1	H_3 ; 7.50
	d,1	H_1 ; 7.78
	m,1	H_9 ; 7.79
2,3,6,8-tetrachloro-	d,1	H_7 ; 7.53
	d,1	H_9 ; 7.77
	s,1	H_4 ; 7.78
	s,1	H_1 ; 7.99

continued.......

Table 4 (continued)

Dibenzofuran	Peak Pattern or Type and Number of Protons[a]	Acutal Protons Involved[b] and Chemical Shift (ppm)[c]
2,4,6,8-tetrachloro-	d,2	$H_3 + H_7$; 7.52
	d,2	$H_1 + H_9$; 7.74
2,3,7,8-tetrachloro-	s,2	$H_4 + H_6$; 7.72
	s,2	$H_1 + H_9$; 7.99
1,3,4,7,8-pentachloro-	s,1	H_2 ; 7.46
	s,1	H_6 ; 7.78
	s,1	H_9 ; 8.30

[a] s - singlet, d - doublet, t - triplet, m - multiplet

[b] where assigned in the literature (see ref. 1, 2 and 4)

[c] relative to TMS

1.1.4 Gas Chromatographic Properties

Analysis of contaminant residues in environmental samples usually relies on various isolation techniques (ie. solvent extraction, column partitioning) and ultimate quantitation using gas-liquid chromatography (GLC). GLC coupled with mass spectrometry (MS) has become the primary technique used in structure confirmation.

GLC, using open-tubular packed columns, separated the PCDDs [2,12,13,14] and the PCDFs [4,12,13,14,15] according to chlorine content but showed little selectivity towards individual isomers. In most cases the retention times increased with increasing chlorine content. In the case of the PCDFs, chlorine substitution ortho to the ring oxygen, that is in the 4 and 6 positions, tends to decrease the retention time of the individual isomers.[14] A similar effect has been seen with individual PCDD isomers on glass capillary columns.[3] Generally the retention times of the PCDDs and PCDFs were in the same range as the PCBs and most of the common chlorinated pesticides.[15]

Glass capillary columns have been found to successfully resolve individual PCDD and PCDF isomers[16] (eg. 8 of 10 tetrachloro PCDD isomers). As with the open-tubular packed columns, the retention times generally increased with increasing chlorine content. On the more polar columns (ie. Silar 10C), the polarity of the isomers had a pronounced influence leading to a reversal of this elution order.

It has been suggested that capillary columns are more applicable to PCDD and PCDF analysis because of their ability to separate isomers. Since only a few of the isomers are of any great interest due to their extreme toxicity, and not all of the possible isomers have been found as contaminants, the packed column GLC approach is still widely used. Recent developments in high resolution packings (ie. the ultrabonded packings), higher detection limits for capillary columns, and time and cost factors also support the continued use of packed columns for contaminant, in particular dioxin and dibenzofuran, analysis.

1.2 BIOLOGICAL AND TOXICOLOGICAL PROPERTIES OF CHLORINATED DIBENZOFURANS (PCDFs) AND CHLORINATED DIBENZO-p-DIOXINS (PCDDs)

This discovery that PCDFs and PCDDs existed as contaminants in commercial compounds, such as PCBs and PCPs, was due primarily to the extreme toxicity of some of their individual congeners. For example, previous research has shown that certain fractions of commercial PCBs were far more toxic to chicks and that these fractions contained PCDFs.[38] In a similar manner, technical pentachlorophenol, containing PCDDs, was found to give positive results for most toxicological tests whereas the changes effected by 'pure' pentachlorophenol were limited to increased liver and kidney weights.[48] A brief discussion of the biological and toxicological properties of PCDFs and PCDDs is given in the following section.

1.2.1 Chlorinated Dibenzofurans (PCDFs)

Most biological studies using PCDFs have investigated only the acute toxicity of these compounds. Few research groups have concerned themselves with the actual mechanisms of toxicity or with metabolism of PCDFs.

1.2.1.1 Metabolism and Biochemical Toxicology

Metabolism

To our knowledge, only one study has actually identified a PCDF metabolite. Zitko and his coworkers[49] were able to isolate a hydroxylated dichlorodibenzofuran from fish which were fed 2,8-dichlorodibenzofuran. The actual structure of this metabolite and its mechanism of formation could not be determined.

In what may be considered 'metabolism-related' research, the tissue clearance of a mixture of PCDFs in mice has been investigated.[50] In this study, it was observed that the PCDFs were primarily concentrated in the liver and fat tissue with a surprisingly high level in the spleen. Gas chromatographic (GLC) patterns of the PCDFs in the livers indicated that certain isomers (usually of lower chlorine content) were not retained as long as others. The authors suggested that this may be due to preferential metabolism and/or excretion of certain isomers. The biological half life of the PCDFs used in mice was estimated to be about one week.

Enzyme Induction and other Biochemical Effects

PCDFs are potent inducers of enzyme systems, particularily in the liver [51,52]. In this respect TCDF has been found to be equipotent with TCDD, 3,4,3',4'-tetrachloroazoxybenzene and 3,4,3',4'-tetrachloroazobenzene in inducing aryl hydrocarbon hydroxylase (AHH). These four compounds compete equally with each other for stereospecific binding sites in the hepatic cytosol which are thought to be the receptor sites for the induction of this enzyme.

Many other biochemical effects were reported when rats were fed diets containing 1 or 10ppm of PCDFs. These included increased serum cholesterol levels and cholinesterase activity and decreased triglyceride levels and leucine aminopeptidase activity. PCDFs also decreased serum glutamic-pyruvic transaminase activity and testosterone concentrations in the testes and increased serum glutamic oxaloacetic transaminase activity.

1.2.1.2 Toxicology

Animals

The toxicity of individual PCDFs is extremely dependent upon the degree and position of chlorination and seems to peak at the tetra and pentachlorodibenzofurans. The most toxic congeners are the 2,3,7,8-tetra-,1,2,3,7,8-penta- and 2,3,4,7,8-pentachlorodibenzofuran[53], while it is presently proposed that dibenzofuran itself or octachlorodibenzofuran have little inherent toxicity on an acute basis.

In 1961 Bauer et al[54] observed that a single oral dose of 0.5 mg/kg of a mixture of tri- and tetrachlorodibenzofurans given to rabbits caused severe and often fatal liver necrosis. The single oral LD_{50} for TCDF for guinea pigs has been determined to be between 5 and 10ug/kg. The symptoms of toxicity were severe weight loss and atrophy of the thymus and spleen. Hemorrhages were observed in the adrenals, urinary bladder and single cell necrosis was noted in the liver.[55] The oral LD_{50} for mice for a mixture of PCDFs was found to be approximately 200mg/kg for males, and 400mg/kg for females. In the mice that died, hepatomegaly and atrophy of the thymus were the more common manifestations; subcutaneous edema and dermal alterations were also observed frequently.[56] TCDF (6mg/kg) administered subcutaneously to mice produced similar symptoms but no deaths.[55] Rats fed diets containing 10 ppm of a PCDF mixture over 4 weeks developed chloracne type lesions and showed toxic effects similar to those in mice.[57]

As yet, there have been no long term or subacute toxicity studies using PCDFs. The reproductive effects of these compounds also remain to be investigated.

Human

Human injestion of only PCDFs has not yet been reported. However, in Japan, over 1000 people consumed rice oil contaminated with PCB[58] and developed nausea, lethargy, subcutaneous edema of the face, and chloracne. It was subsequently demonstrated that the rice oil injested was more than twice as toxic as it should be with the amount of PCB present.[59] In addition it was later determined that this PCB contaminated rice oil contained large amounts of PCDFs.[60] Whether these symptoms of the poisoning are due solely to PCBs (i.e. and not in part to PCDFs) is as yet indeterminable.

1.2.2 Chlorinated Dibenzo-p-dioxins (PCDDs)

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) is one of the most toxic compounds known to man. PCDDs have received considerably more attention than the PCDFs, however, their toxicological properties can, in most cases, be considered to parallel one another.

1.2.2.1 Metabolism and Biochemical Toxicology

Metabolism

^{14}C-TCDD fed to rats was found to be rather incompletely adsorbed from the gastrointestinal tract, with the majority ending up in the fesces. Once absorbed in the body, most of the TCDD accumulated in the liver and fat. The level in these tissues was nominally ten times higher than in other tissues. Traces of radioactivity were also detected in the urine and expired air of the rats within the first 10 days; whether this was metabolized or unaltered TCDD was not determined.[64,65]

TCDD has been considered by most groups to be resistant to metabolism by mammals, in vivo and in vitro.[61,62] Recently, however, Tulp and Hutzinger[63] have found that several PCDDs (although not including TCDD) were metabolized by rats to mono- and dihydroxy derivatives. In the case of the monochloro and unsubstituted dibenzo-p-dioxin, sulfur containing metabolites were also detected. Primary hydroxylation was determined to take place at the 2-, 3-, 7-, or 8-positions in the molecule and it was suggested that an intermediate 2,3-epoxide was involved. Since in TCDD these positions are blocked, this was felt to be a viable reason for this chemical's resistance to metabolism.

Enzyme Induction and other Biochemical Effects

Some of the PCDDs have been reported to be powerful inducers of the enzymes δ-aminolevulinic acid synthetase (ALAS) and aryl hydrocarbon hydroxylase (AHH) in the chick embryo.[51,66] The potency of the AHH induction was shown to strongly correlate with general toxic responses.[67]

For AHH[68] and ALAS[69] induction, the activity of the individual PCDD congeners has been found to be strongly dependent on the position of chlorine substitution; at least three halogens are required in lateral (2-,3-,7- and 8-) positions with at least one hydrogen remaining on the dioxin nucleus.

The highest potency, shown by TCDD, for inducing AHH was found to parallel other inducers of similar molecular structure (i.e. TCDF).[52] TCDD is also a strong inducer of a number of other enzymes including rat liver DT-diaphorase[69] and glutathione S-transferase.[70]

In addition, TCDD has been reported to bind to rat hepatic microsomal macromolecules pretreated with phenobaritol (>40% of added ^{14}C-TCDD).[71] Microsomes prepared from noninduced rats bound only 7.0% of the added ^{14}C-TCDD, indicating that the binding of this compound is mediated by a mixed function oxidase system.

Most biochemical changes noted in serum taken from rats fed TCDD (10mg/kg) were attributable to liver damage. For example, the activites of glutamic-oxaloacetic transaminase, glutamic-pyruvate transaminase, lactic dehydrogenase and hydroxybuturate dehydrogenase were elevated, as were the levels of bilirubin, cholesterol and urea. In addition, the rats had decreased serum glucose, sodium and protein levels as well as decreased arylesterase and cholinesterase activities.[72] Mice fed various levels of TCDD were reported to have significantly decreased serum protein[73] and increased liver lipid levels.[74]

1.2.2.2 Toxicology

Animal

The toxicity of individual PCDD congeners is strikingly dependent upon the position and number of chlorine substituents. For example, TCDD is reported to be 1,000 to 10,000 times as toxic as 1,2,3,8-tetrachlorodibenzo-*p*-dioxin. The most toxic PCDDs appear to be the 2,3,7,8-tetra-(TCDD), 1,2,3,7,8-penta-, 1,2,3,6,7,8-and 1,2,3,7,8,9-hexachloro-*p*-dioxins.[6]

The acute toxicity of TCDD has been tested in several animals. In one study the single oral LD_{50} ranged from 0.0006 mg/kg in male guinea pigs to 0.115 mg/kg in rabbits of mixed sex. For male rats the LD_{50} value was determined to be 0.022 mg/kg whereas female rats were less sensitive giving an LD_{50} value of 0.045 mg/kg.[75] The average mean survival time for these rats was ca. 20 days post administration. For male mice the oral LD_{50} was determined to be 0.114 μg/kg with a mean survival time of, again, approximately 20 days. For female Rhesus monkeys it was given to be <0.070 mg/kg with death occurring, on the average, 30 days after injection.[76]

The acute toxicological effects of TCDD common to most of the animals studied, were weight loss (due to a decrease in consumption), increased liver to body weight ratios and decreased thymus to body weight ratios. In mice, TCDD was also found to be porphyrogenic and caused subcutaneous edema, hepatic lesions and hemorrhaging in almost all of the organs.[73] Rhesus monkeys suffered loss of hair and fingernails, gastric ulcers, liver necrosis, facial alopecia and developed chloracne type eruptions as well as the common effects.[76] TCDD was found to be porphyrogenic and also created hepatic and cardiac lesions in rats.[77]

Mice fed TCDD on a subacute basis (1,5 and 25 ug/kg) developed similar symptoms to those in the acute experiment. The most severe lesions were observed in the liver and thymus with a 'no-effect' level reported as a 0.2 ug/kg dose.[73]

In a 13-week oral toxicity study using rats fed TCDD at levels of 0.001, 0.01, 0.1 or 1 ug/kg, 5 days per week [77], doses of 1.0 ug/kg TCDD caused some mortality and toxicological symptoms again similar (although milder) to those observed when an acute dose was administered. At the 0.1 ug/kg TCDD dosage level, somwhat milder toxicological symptoms were again observed but no deaths. In rats given 0.01 or 0.001 ug/kg, TCDD there was essentially no effect.

The results of a 2 year chronic toxicity study of TCDD in rats indicated that continuous doses of TCDD sufficient to induce severe toxicity, increased the incidence of some types of tumors while reducing others. These rats were fed diets supplying 0.1, 0.01 and 0.001 ug of TCDD/kg/day.[78]

PCDDs have also been reported to be embryotoxic when administered prenatally to rats and mice.[79,80] Three major teratogenic effects have been noted; these are:

- intestinal hemorrhages in rat fetuses
- an increased frequency of cleft palate in mouse fetuses
- kidney abnormalities in mouse fetuses.

Of the PCDDs, TCDD, as expected, is the most active with the hexachloro derivatives showing some activity. The di- and octachloro isomers were reported to be nonembryotoxic. Generally, it has been shown that embryotoxic activity is also a property of those PCDDs that have a pronounced chloracne potency.

Human

Accidental releases of PCDD into the environment have occurred in the U.K., U.S.A., Germany, Holland and, most recently, in Seveso, Italy. All of these occurences have been well documented as have the toxicological effects in exposed humans.

The most common initial symptom of dioxin poisoning in humans is severe skin disease (chloracne). Other symptoms which have been observed and attributed to PCDD poisoning are liver cirrhosis, damage to the heart, kidney, spleen, central nervous system and pancreas, and emphysema. As well as these physiological symptoms, psychological effects such as depression and disturbances of memory and concentration have also been observed. Several deaths from TCDD poisoning have been recorded, at least some as a result of liver damage and some many years after exposure.

1.3 PCDDs AND PCDFs IN PCB-BASED ELECTRICAL FLUIDS AND OTHER COMMERCIAL COMPOUNDS

1.3.1 PCDDs and PCDFs in Chlorophenols and their Derivatives

Chlorophenols, in particular pentachlorophenol (PCP), and their derivatives are used in large quantities as herbicides, slimicides in paper mills and as wood preservatives. These compounds have been found to contain a variety of contaminants including other chlorophenols, polychlorinated phenoxyphenols (PCPPs), polychlorinated diphenylethers (PCDPEs), polychlorinated biphenyls (PCBs) and polychlorinated benzenes (PCBzs).[18,19] Of major interest and concern is that they also contain significant quantities of chlorinated dibenzo-*p*-dioxins and dibenzofurans.

A survey of various commercial PCPs and their sodium salts by Buser and Bosshardt[20] revealed that levels of PCDDs and PCDFs varied from 1 to 2 ppm to as high as 200 to 300 ppm. In these samples the major components present were the hepta- and octachloro congeners. Levels of the tetra- and pentachloro congeners were generally less than 0.1 ppm in all the preparations tested. Similar results were observed by other researchers[12,21] with even higher levels of PCDDs and PCDFs being reported[22,23]. Analysis of the lower chlorinated chlorophenols and their sodium salts showed correspondingly higher levels of tetra-and pentachlorodibenzo-*p*-dioxins and dibenzofurans and lower levels of the hepta-and octachloro components, as would be anticipated.[24]

PCDD and PCDF formation in chlorophenol preparations has been studied extensively[3,23,24] and these compounds, or their precursors, are formed by thermal dimerization of the chlorophenates. Experimental pyrolysis of commercial chlorophenols and sodiumchlorophenates has been shown to give increased levels of PCDDs and PCDFs only with the chlorophenates.[25,26] The formation of the PCDFs is believed to be due to cyclization of an impurity in the commercial product rather than the chlorophenate itself. The polychlorinated diphenyl ethers are presumably the most likely precursors of the PCDFs since they are known contaminants of the chlorophenols and their pyrolysis has been found to yield dibenzofurans.[9]

It has also been determined that PCDDs are formed by a unimolecular cyclization of chlorinated phenoxyphenols (PCPPs). These "predioxins" have been found in technical PCP preparations[27,28] and individual PCPPs are known to cyclize giving dioxins.[19] Photochemical dimerization of chlorinated phenols[29] and cyclization of PCPPs[30,31] are also potential sources of PCDDs in chlorophenols.

1.3.2 PCDDs and PCDFs in 2,4,5-T Preparations

Herbicides derived from 2,4,5-trichlorophenoxy acids (2,4,5-T) have received considerable attention recently due to their contamination by dioxins and dibenzofurans. PCDDs and PCDFs have been identified in various 2,4,5-T ester formulations[32,33] such as 'Herbicide Orange', a defoliant used in Vietnam in the late 1960's[32,34].

Analyses carried out in the more recent of these surveys showed that the phenoxy acids were primarily contaminated by PCDDs, with PCDFs identified in only a few of the samples.[32] These results differ somewhat from previous research[33] but this is most likely due to the samples chosen for testing.

In burning experiments with 2,4,5-T esters, and also its sodium salt, no 2,3,7,8-tetrachlorodibenzo-_p_-dioxin was formed.[6,35] Although other researchers have suggested that combustion of 2,4,5-T formulation may lead to formation of small amounts of PCDDs and PCDFs,[33] this route is not an important source of these contaminants as it was with the chlorophenates. Similarily the primary photoreactions of chlorinated phenoxy acids are dechlorination and hydroxyl substitution of the chlorines, with no formation of PCDDs or PCDFs occurring.

1.3.3 PCDDs and PCDFs in Fly Ash and Flue Gas

There is growing public concern over the presence of hazardous organic compounds in the emissions from municipal incinerators, thermal generating stations and various heating facilities. Olie,[13] and his coworkers first reported the detection of PCDDs and PCDFs as trace components of the fly ash and flue gases of three incinerators in the Netherlands. They also found that the major chlorinated compounds in all the fly ash samples were highly chlorinated benzenes, whereas in flue gas condensates, the most abundant chlorinated hydrocarbons were the chlorinated phenols. At this time they suggested that these phenols were most likely the major precursors for the PCDDs and PCDFs detected.

Similar surveys were performed in Switzerland using fly ash samples collected at a municipal incinerator and at an industrial heating facility.[36,37] Both PCDDs and PCDFs were found in these samples. The PCDD compounds detected were similar to those formed when a 2,4,6-tri-,2,3,4,6-tetra- and pentachlorophenate mixture was pyrolyzed under controlled laboratory conditions.[36] Most of the PCDF congeners detected in the fly ash were also identified in experimental pyrolyses of commercial PCBs.[37]

1.3.4 PCDFs in PCB-Based Fluids

Vos, and his coworkers where the first to identify PCDFs as toxic impurities in two samples of European commercial PCBs. (Clophen and Phenoclor). The toxic effects of the PCBs were found to parallel the levels of the PCDFs present.[38] The Japanese PCB preparation, Kanechlor 400, which had been identified as the causative agent of Yusho (a human PCB poisoning incident), was also found to be contaminated with PCDFs.[39] Bowes and his associates were able to identify PCDFs in a number of American PCBs (see Table 5)[40], in particular the 2,3,7,8-tetrachloro isomer.[15] They also examined the two European PCBs previously analyzed by Vos[38] and found that these PCBs contained at least 10 times more PCDFs than the corresponding Aroclors.

Recently Morita et al[41] identified PCDFs in 16 PCB preparations of various origin and also in the Yusho oil (rice bran oil) responsible for the PCB poisoning. This oil was later analyzed by high resolution GC/MS and it was found that the main PCDF contaminant was the 2,3,7,8-tetrachloro isomer.[42]

Table 5 PCDFs in Aroclor, Clophen and Phenoclor (ppm)[40]

PCB	Chlorodibenzofurans			TOTAL
	Cl_4	Cl_5	Cl_6	
Aroclor 1248 (1969)	0.5	1.2	0.3	2.0
Aroclor 1254 (1969)	0.1	0.2	1.4	1.7
Aroclor 1254 (1970)	0.2	0.4	0.9	1.5
Aroclor 1260 (1959)	0.1	0.4	0.5	1.0
Aroclor 1260 (lot.AK3)	0.2	0.3	0.3	0.8
Aroclor 1016 (1972)	ND	ND	ND	-
Clophen A-60	1.4	5.0	2.2	8.4
Phenoclor DP-6	0.7	10.0	2.9	13.6

There has been some indication that PCBs also contain minor amounts of penta- and hexachloro dibenzo-*p*-dioxins (approximately 3% relative to the corresponding PCDF).[6] The levels of these additional contaminants, if they are indeed present, are insignificant compared to the levels of the PCDFs.

1.3.5 Formation of PCDFs from the Pyrolysis of PCBs

High temperature destruction of PCBs at present appears to be the most efficient and less costly method of disposing of these chemicals. The pyrolysis of PCBs has been tested using various laboratory-scale systems. Vapour injection of PCBs into high temperature air environments (1 second dwell time) resulted in greater than 95% destruction at 740°C, and 99.995% at 1000°C forming only low molecular weight compounds (as yet unidentified).[43] Atomizing PCBs with oxygen using a burner and igniting this mixture (giving a flame temperature over 2000°C) resulted in >99.99999% destruction.[44]

On a larger scale, PCBs mixed with other halogenated hydrocarbons were burned in a rotary cement Kiln.[45] The effective temperature was reported as 2100°C or higher. In this case the PCBs were destroyed with at least, a 99.98% efficiency with no high molecular weight chlorinated hydrocarbons being emitted.

It thus has generally been determined that at temperatures greater than 700°C pyrolysis of PCBs is virtually complete giving only low molecular weight compounds. At temperatures lower than 700°C, with oxygen present, a significant amount of the PCBs are converted to PCDFs.

Morita and his associates[41] found increased amounts of PCDFs in Aroclor 1248 when it was sealed with air in a glass tube and heated at 300°C for two weeks. They also analyzed a Japanese PCB mixture that had been used in a heat exchange system for long periods of time and discovered that it too contained higher levels of PCDFs than in the unused oil.

Pyrolysis of Aroclor 1254 at 550-650°C in quartz ampoules in the presence of air by Buser et al[37,46] showed the formation of up to 60 PCDF components ranging from the mono- to the pentachloro compounds at a combined level of about 1-3%. In addition to PCDFs, polychlorinated hydroxybiphenyls were identified as possible precursors. The pryolysis of Aroclor 1260 showed the formation of PCDFs at a similar level as in the case of Aroclor 1254. The compounds formed ranged from the tri- to the heptachloro congeners.

Buser and his coworkers also investigated the pyrolysis of individual PCB isomers and found that they yielded PCDFs through the formal loss of orthoCl$_2$ or HCl. For example, the pyrolysis of 2,4,5,2',4',5'-hexachlorobiphenyl yielded three PCDFs as shown in Figure 5.

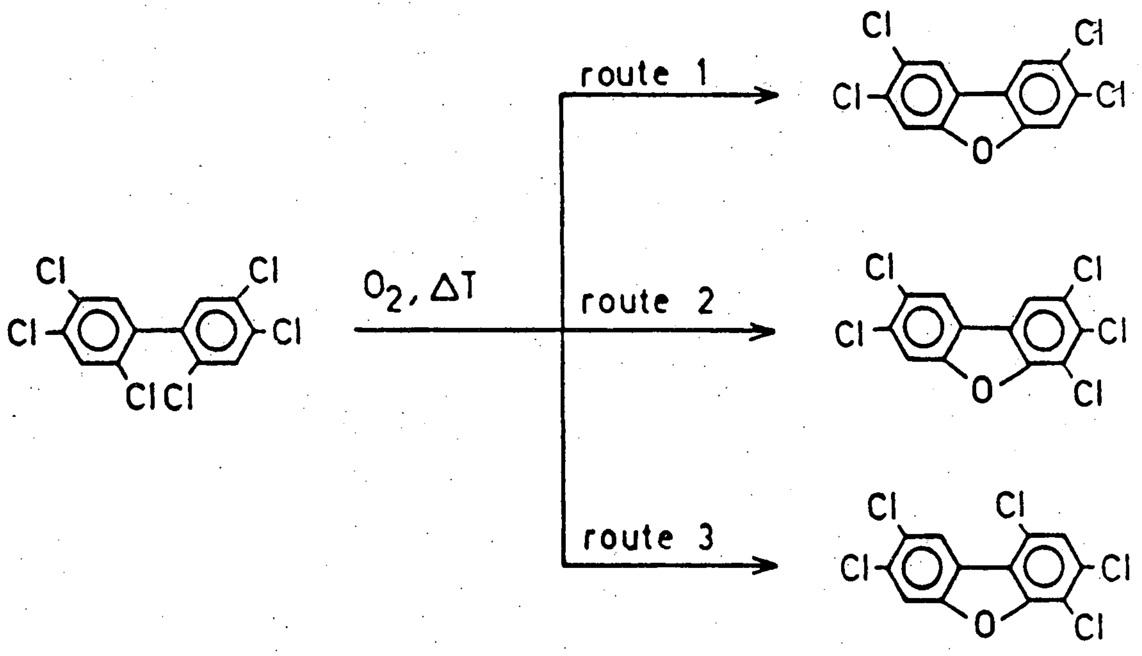


Figure 5: Pyrolysis of 2,4,5,2',4',5'-Hexachlorobiphenyl

The formation of PCDFs from the pyrolysis of PCBs may have environmental complications because a large portion of used PCBs may be disposed of by way of incineration. If the proper conditions are not used this may become a potential source of PCDF contamination. A recent fire in Toronto involving a PCB filled transformer illustrates this risk. This accident released PCBs and soot containing appreciable levels of PCDFs into the atmosphere.[47] The thermal conversion of PCBs into PCDFs may also occur in askarel filled transformers while in service. This possibility is investigated as part of this project and will be discussed later.

2 CHLORINATED DIBENZOFURANS (PCDFs) AND CHLORINATED DIBENZO-P-DIOXINS (PCDDs) IN PCB-BASED FLUIDS USED IN ELECTRICAL EQUIPMENT

2.1 INTRODUCTION

Under current federal regulations, PCBs can only be used in electrical and some mechanical equipment currently in service. Proposed PCB regulations will prohibit new PCB containing equipment being imported or manufactured for use in Canada. Due to these regulations, PCB filled transformers and capacitors that come out of service will be replaced by equipment using fluids that do not contain PCBs (e.g. silicone based fluids).

At the present, there are many PCB or Askarel filled units in service and it is anticipated that some of these will still be in use 40 to 50 years from now. During the interim period, PCBs will therefore still pose a threat to environmental quality unless properly handled and eventually destroyed. One of the newer problems associated with these fluids is their possible contamination by PCDFs and PCDDs.

The purpose of this portion of the project is to investigate the formation of PCDFs and PCDDs in PCB based fluids that are being used in electrical equipment. The ultimate aim of this study is to ascertain those conditions which change the basic composition of these fluids, particularly with respect to the formation of these potentially toxic impurities.

2.2 EXPERIMENTAL

2.2.1 Sampling of PCBs in Electrical Equipment

2.2.1.1 Introduction

At the beginning of this project it was intended that both transformers and capacitors would be sampled. Capacitors, though, were found to be inappropriate for this study because of three major problems:

1) due to their location (i.e. pole mounted usually) they were too difficult to sample,

2) there was very little information on the sealed units, and,

3) they could not be sampled while in service.

Because of these problems all of the sampling was restricted to electrical transformers. A brief discussion of transformers, their use and construction, is given in Appendix A. Details of the transformer sampling are given in the following sections.

2.2.1.2 Transformer Askarel Sampling

2.2.1.2.1 Sampling Criteria

Initially it was proposed that a variety of electrical transformers would be sampled with respect to a single variable; that is, keeping all others constant. The variables chosen were:

1) the type of PCB containing fluid or Askarel.

2) the length of time in service

3) the power rating

4) the load

5) the length of time in service since maintenance

6) malfunctions (i.e. arcing)

7) the volume of fluid in the unit

Later in the project, it became apparent from existing transformer inventories that some of these variables could not be isolated. In most cases, there were no records as to the load under which the transformers were operated or whether they had been taken out of service for maintenance or retrofilling. It was also determined that the power rating (kva) and the fluid volume could not be totally isolated as separate variables since the fluid volume is generally increased as the kva increases. The sampling was also limited to step-down, power transformers (see Appendix A). The available transformers were thus sampled in groups as described below.

2.2.1.2.2 Transformer Askarel Sample Groups (see Table 6)

Group 1 : Time In Service (1-1, 1-2, etc.)

The first series of transformers sampled were those where the only variable was the length of time since they had been installed. The transformers sampled were all from the same manufacturer and it was therefore assumed that they contained the same fluid (see Section 2.2.1.2.4). These transformers were rated at 1500 kva and had essentially identical kva/volume ratios.

Group 2 : Variable kva/volume Ratio (2-1, 2-2, etc.)

Although as previously mentioned, the kva and fluid volume of a transformer are interdependant, there is some variation in the kva/volume ratio (see Table 6). For each of two fluids, Pyranol and Chlorextol, four transformers were sampled where the only variable was this ratio.

Group 3 : Variable Type of Fluid (3-1, 3-2, etc.)

As discussed in the Appendix, there are three major askarels (chlorobenzene-PCB mixtures) currently in use in transformers in Canada. In this sample group, two sets of three transformers were sampled. The only difference between the two sets was the kva/volume ratio. Essentially, the only variable distinguishing the three transformers from each other in each set was the type of fluid they contained (i.e. Inerteen, Pyranol or Chlorextol).

Group 4 : (4-1, 4-2, etc.)

In this group askarels were sampled from transformers which were operated under what may be considered extreme conditions. Samples 4-1 and 4-2 were taken from two transformers which had been in service since 1947. Sample 4-1 was taken from a 56 kva transformer with a fluid volume of 660 liters. Sample 4-2 was taken from a 10,000 kva transformer with a fluid volume of 6900 liters. The difference in kva between 4-1 and 4-2 is quite large when compared to the change in volume. These two samples could therefore be considered to approximate the effect of variable kva.

Samples 4-3 and 4-4 were taken from transformers which had failed while in service; 4-3 from a transformer which failed and caused a fire (Adelaide St.), and 4-4 from a transformer which overheated (Walkerton). Also included in this group are samples of unused Pyranol, Inerteen and Chlorextol (samples 4-5, 4-6 and 4-7 respectively).

2.2.1.2.3 Collection of Askarel Samples

Almost all of the askarel samples were taken from the top valve on the transformer. In a few cases the fluid levels were too low and the bottom valve had to be used for sampling. All the samples were collected in prewashed, 250 ml amber glass bottles fitted with teflon-lined screw caps. The askarel samples were stored at ca. 0°C. in the dark until analyzed.

2.2.1.2.4 Determination of Chlorobenzene/Polychlorinated Biphenyl (PCBz/PCB) Ratio

Transformer askarel fluids are mixtures of various chlorobenzenes and PCBs. The PCBz/PCB ratios given by the manufacturer for the three major fluids, Pyranol, Inerteen and Chlorextol (see Appendix A) are only approximate values and may vary from transformer to transformer. The exact PCBz and PCB content of each askarel sample was therefore determined by gas chromatography. Since the composition of the Aroclors (1254 and 1260) may vary from batch to batch, the chlorobenzene content was determined and the remainder assumed to be PCB. The type of Aroclor used in the mixture was determined by comparing the chromatographic pattern of the PCB component to that of the pure Aroclors (1254 and 1260). The actual method used for this determination is as follows:

Method : A known weight of each askarel sample was dissolved in petroleum ether to give a concentration of 10.0 ± 0.01 mg/ml. Standard solutions of each tri-, tetra- and pentachlorobenzene (2.0 ± 0.01 mg/ml) were also prepared in petroleum ether. The PCBz content of each askarel sample was then determined by comparing duplicate 5 μℓ GLC/FID injections of the PCBz solutions to those of the askarel solutions.

GLC/FID was performed using a Hewlett Packard 5710A instrument equipped with a flame-ionization detector (FID). The column used was a 4' x ¼" glass column packed with 3% OV-225 on Gas Chrom Q. The oven was operated isothermally at 125°C for 8 minutes and then temperature programmed to 220°C at 8° per minute. The carrier gas used was helium at 40 ml/min. and the detector and injection port temperatures were set at 250°C. All chromatographic data was recorded on a H-P 3380S integrator.

2.2.2 Analysis of Askarel Samples for PCDFs and PCDDs

2.2.2.1 Introduction

A review of the literature indicated that PCDFs are the major contaminants of PCBs. If any PCDDs were present in previous analyses, their levels were considered relatively insignificant. In this experimental section of the project, the fraction of the askarels containing the PCDFs and PCDDs was first isolated using Florisil and alumina. This fraction was then analyzed for PCDFs and PCDDs and other contaminants.

2.2.2.2 Isolation of PCDFs and PCDDs from Askarels

Duplicate samples of each askarel collected in section 2.2.1 were fractionated on Florisil and alumina columns as described by Roach and Pomerantz.[39] The revised method used in this project is given as a flow chart in Figure 6. All solvents used were pesticide grade.

In this procedure, 500 mg of the askarel was first dissolved in petroleum ether and applied to the top of a glass column (25 cm x 1 cm.i.d.) packed with Florisil(PR-60/100; Applied Science) which had been previously washed with petroleum ether (50 ml). The column was then eluted, first with 100 ml of petroleum ether, then with 50 ml of a 5% ether/petroleum ether mixture, and finally with 50 ml of a 25% ether/petroleum ether mixture. The second eluate was evaporated just to dryness, and the residue remaining was then quantitatively transferred, using petroleum ether (ca. 2 ml), to the top of a second column (15 x 0.5 cm i.d.) packed with alumina (neutral, activity 1, 80/200 mesh) which had been prewashed with 2% methylene chloride/petroleum ether (15 ml). This column was then eluted first with 2% methylene chloride/petroleum ether (15 ml) and then with 50% methylene chloride/petroleum ether (15 ml). The second eluate from this column was evaporated just to dryness, reconstituted with petroleum ether (5 ml) and then again evaporated to dryness. For gas chromatographic-mass spectrometric (GC/MS) analysis the residue was redissolved in exactly 1 ml of toluene. For gas chromatographic analysis, using an electron capture detector (GLC/ECD), the residue was reconstituted with exactly 1 ml of isooctane.

The recovery of this isolation procedure was tested using Aroclor 1254, previously purified on a Florisil column, spiked with 0.01, 0.001 and 0.0001 mg of 2,3,7,8-tetrachlorodibenzofuran.

what was the recovery

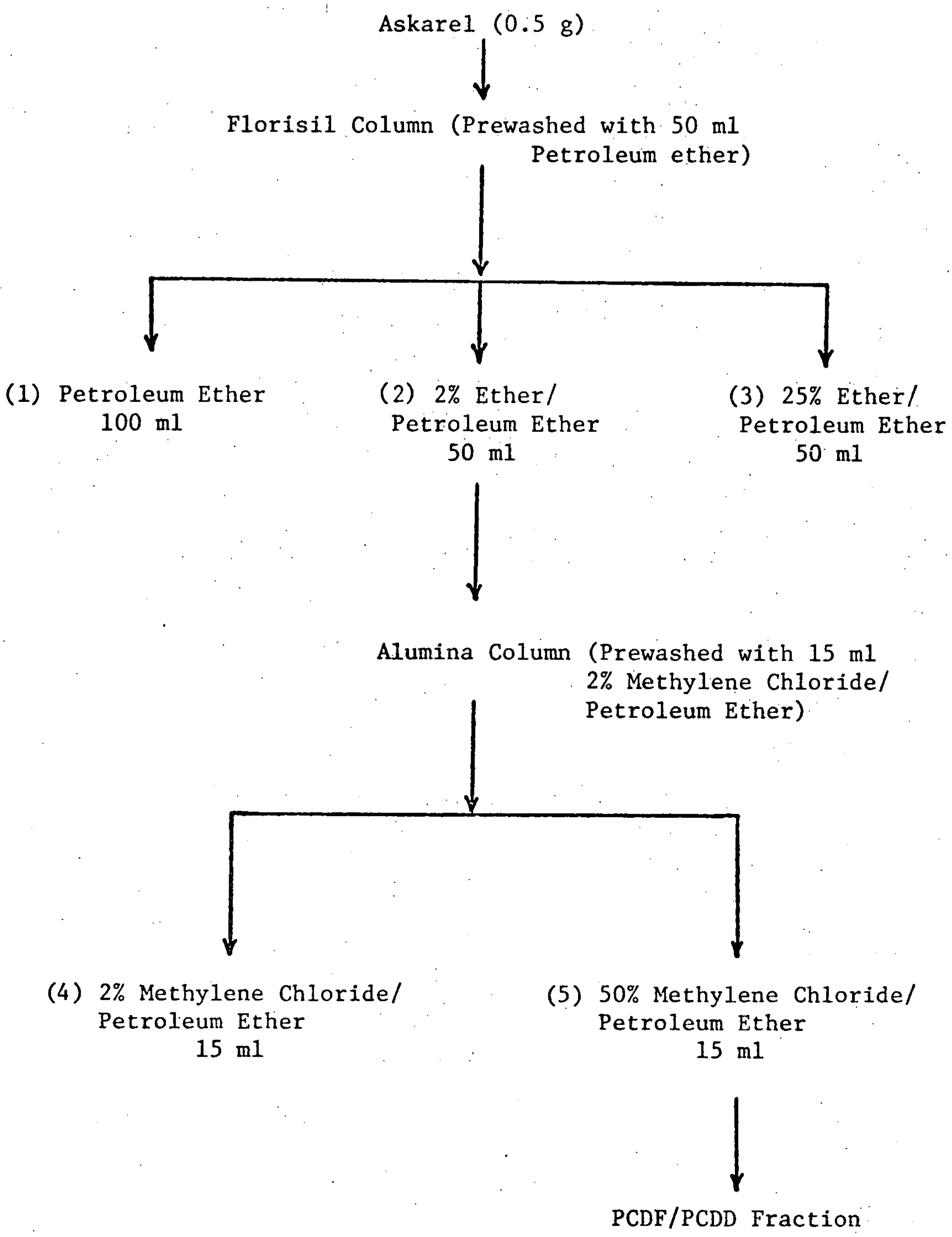


Figure 6 : Isolation of PCDF/PCDD Fraction from Askarel

2.2.2.3 Analysis of PCDF/PCDD Fraction using Gas Chromatograph/Mass Spectrometry (GC/MS)

GC/MS was carried out on a Hewlett-Packard 5980 A instrument. The GLC column used was a 6 ft. x 2 mm i.d. glass column filled with 0.2% Carbowax 20M on Chromosorb W 100-120 mesh (Aue or Ultrabond). Helium was used as the carrier gas at a flow rate of ca. 30 ml/min. The injection temperature was 250°C. and the oven temperature was kept at 170°C for 2 minutes and then temperature programmed to 240°C at 8° per minute. For the interface, a jet seperator was used at 350°C. The ion source temperature was 215°C and the temperature of the analyzer was set at 110°C. A 70 ev electron energy was used with the scan rate set at 160 amu/sec.

The PCDF/PCDD fraction dissolved in toluene (1 ml) was injected into the GLC portion of the instrument. The mass spectra and the ion current were then monitored as the individual components eluted into the mass spectrometer. Individual ions were monitored by operating the GC/MS in the Single Ion Monitoring (SIM) mode.

2.2.2.4 Analysis of the PCDF/PCDD Fraction for PCDF

Due to the results obtained from initial GC/MS analyses of the PCDF/PCDD fractions obtained in section 2.2.2.2 (see Results) these fractions were subsequently only analyzed for PCDFs, in particular 2,3,7,8-tetrachlorodibenzofuran (TCDF).

2.2.2.4.1 Determination of Total PCDF by Perchlorination

To analyze the PCDF/PCDD fraction for total PCDF the perchlorination method, as described by Hutzinger et. al.,[81] was used. The sample to be perchlorinated was transferred using petroleum ether to a glass stoppered test tube. The petroleum ether was then removed by evaporation using a hot water bath and

N$_2$ gas flashing. To further insure that all traces of the petroleum ether were removed, three successive additions and evaporations of methylene chloride (2 ml) were made. The perchlorination reagent (BMC; 1 ml; see paper by Hutzinger et.al.,[59]) was then added to the residue, the test tubes loosely capped with foil and the reaction mixture heated at ca. 69°C for 2 hours. 25% hydrochloric acid (3 ml) was then added and the resultant solution heated for one hour at 70 to 80°C. The final solution was then allowed to cool to room temperature and was then extracted twice with petroleum ether (2 x 10 ml) or another suitable solvent. These extracts were then washed, first with distilled water (5 ml) and then with 10% sodium bicarbonate (5 ml), and then evaporated just to dryness using N$_2$ gas flashing. The residue remaining was dissolved in exactly 1 ml of isooctane and then analyzed by gas chromatography.

Gas-liquid chromatography (GLC/ECD) was performed using a Hewlett-Packard 5710A chromatograph equipped with a Ni^{63} electron capture detector (ECD). The column used was a 4 ft. x 4 mm i.d. glass column packed with 3% OV-101 coated on Ultrabond (or Aue; 0.2% Carbowax 20M on Chromosorb W 100/120). The carrier gas used was Argon/Methane (5%) at 60 ml/min. The detector temperature was set at 300°C. The oven and injection port were operated isothermally at 240°C.

The percent recovery and perchlorination efficiency of this method was tested using 0.01, 0.001 and 0.0001 mg samples of dibenzofuran and then comparing theoretical and actual amounts of octachlorodibenzofuran formed.

what was it?

2.2.2.4.2 Analysis of PCDF/PCDD Fraction for 2,3,7,8-Tetrachlorodibenzofuran (TCDF)

The amount of TCDF in the askarel samples was determined by analyzing the PCDF/PCDD fraction isolated in section 2.2.2.2 using GLC/ECD. The chromatographic conditions used were the same as those described earlier in section

2.2.2.4.1 except the oven and injection port temperatures were operated isothermally at 225°C.

Quantitation of TCDF was carried out by comparing the peak areas of standard solutions of TCDF (courtesy of Dr. C. Rappe) to those of the peak occurring at the same retention time in the PCDF/PCDD fractions (duplicate 2 ul injections). The amounts of TCDF found were then converted to a ppm value on the basis of 0.50 grams of askarel analyzed.

2.3 RESULTS

2.3.1 Sampling of Transformer Grade Askarels

The data on the transformers sampled and on the askarels they contain is summarized in Table 6. The samples are divided into groups and coded according to the scheme outlined in section 2.2.1.2.2. In the time-in-service study (group 1), three samples were taken from three separate, but identical, transformers for comparison purposes.

It should be noted at this time that the dielectric strength of each of the askarels sampled is also included in this table (most recent measurement available). The dielectric strength, as discussed in Appendix A, is a good indicator of contaminants or decomposition of the askarel (i.e. the lower the dielectric rating the higher the contaminants).

The chlorobenzene and PCB content of each of the askarels sampled are also given in Table 6. Generally it was found that the newer askarels had a higher PCB content (ca. 70%) and those used since 1970 contained Aroclor 1254 rather than Aroclor 1260. The major individual chlorobenzenes found in all these fluids were the 1,2,4- and 1,2,3-tri- and the 1,2,3,4-tetrachlorobenzenes. Small quantities of the other tri-, tetra- and pentachlorobenzene congeners were also detected in most samples. As an example of the analyses,

Table 6: Transformer Data, Askarel Composition and TCDF Concentration

Sample	Installation	Manufacturer	Dielectric Strength (kv)	Power (kva)	Volume (litres)	kva/volume	1,3,5-Cl_3Bz	1,2,4-Cl_3Bz	1,2,3-Cl_3Bz	1,2,3,5- & 1,2,4,5-Cl_4Bz	1,2,3,4-Cl_4Bz	1,2,3,4,5-Cl_5Bz	PCBz/PCB ratio	Aroclor	TCDF
Group 1															
1-1	1957	FP	36	1500	1888	0.79	tr	26.4	6.8	1.0	14.4	2.4	51.0/49.0	1260	0.780
1-2	1961	FP	36	1500	2093	0.72	tr	28.4	6.6	tr	15.2	3.4	53.6/46.4	1260	1.110
1-3	1963	FP	36	1500	1251	1.19	tr	27.8	6.2	tr	14.0	2.6	50.6/49.4	1260	1.020
1-4	1963	FP	36	1500	1251	1.19	tr	28.8	6.4	tr	14.4	2.8	52.4/47.6	1260	0.790
1-5	1963	FP	36	1500	1274	1.17	tr	28.4	8.0	tr	2.2	tr	38.6/61.4	1260	0.350
1-6	1965	FP	29	1500	1151	1.30	tr	28.0	7.6	tr	1.6	ND	37.2/62.8	1260	0.290
1-7	1970	FP	30	1500	1765	0.85	tr	22.6	7.0	tr	tr	ND	29.6/70.4	1254	0.550
1-8	1970	FP	22	1500	1490	1.01	tr	21.2	6.8	tr	tr	ND	28.0/72.0	1254	0.470
1-9	1971	FP	28	1500	1490	1.01	tr	21.2	7.8	tr	tr	ND	29.0/71.0	1254	0.290
1-10	1974	FP	28	1500	1490	1.01	ND	21.6	6.8	ND	ND	ND	28.4/71.6	1254	0.051
1-11	NEW	FP	-	1500	-	-	tr	20.8	9.8	tr	tr	ND	30.6/69.4	1254	0.041
Group 2															
2-1	1967	CGE	33	500	725	0.69	ND	21.4	5.6	tr	14.8	3.4	45.2/54.8	1260	0.030
2-2	1967	CGE	31	1000	938	1.07	tr	26.2	7.2	tr	14.8	3.2	44.3/55.7	1260	0.004
2-3	1967	CGE	36	1000	770	1.30	tr	26.0	7.0	tr	14.4	3.2	50.6/49.4	1260	0.007
2-4	1967	CGE	36	1866	1268	1.47	tr	26.4	6.4	tr	13.4	2.8	49.0/51.0	1260	0.010
2-5	1965	FP	36	700	660	1.06	tr	27.6	7.8	tr	tr	tr	35.4/64.6	1260	0.176
2-6	1965	FP	36	1500	1251	1.20	tr	27.0	5.8	tr	13.6	2.6	49.0/51.0	1260	0.435
2-7	1965	FP	36	2500	2084	1.20	tr	27.8	6.6	tr	1.0	tr	35.4/64.6	1260	0.110
2-8	1965	FP	36	2500	1092	2.29	tr	28.4	8.2	tr	tr	tr	36.6/63.4	1260	0.141
Group 3															
3-1	1967	CGE	33	500	725	0.69	ND	21.4	5.6	tr	14.8	3.4	45.2/54.8	1260	0.419
3-2	1967	CGE	41	1000	770	1.30	tr	26.0	7.0	tr	14.4	3.2	50.6/49.4	1260	0.341
3-3	1967	W	41	750	883	0.85	tr	28.2	8.0	tr	tr	tr	36.2/63.8	1260	0.444
3-4	1967	W	41	1200	1087	1.10	tr	27.4	7.8	tr	tr	tr	35.2/64.8	1260	0.426

continue

Table 6 (continued)

Sample	Installation	Manufacturer	Dielectric Strength (kv)	Power (kva)	Volume (litres)	kva/volume	1,3,5-Cl_3Bz	1,2,4-Cl_3Bz	1,2,3-Cl_3Bz	1,2,3,5- & 1,2,4,5-Cl_4Bz	1,2,3,4-Cl_4Bz	1,2,3,4,5-Cl_5Bz	PCBz/PCB ratio	Aroclor	TCDF
3-5	1967	FP	31	750	829	0.90	tr	28.0	7.8	tr	tr	tr	32.8/67.2	1260	0.168
3-6	1967	FP	36	1000	838	1.19	tr	25.0	7.8	tr	tr	tr	32.8/67.2	1260	0.179
Group 4															
4-1	1947	CGE	-	56	660	0.08	ND	24.8	7.2	tr	14.2	3.0	49.2/50.8	1260	4.730
4-2	1947	CGE	-	10,000	6,900	1.45	ND	25.2	6.6	tr	14.0	2.6	48.4/51.6	1260	2.201
4-3	1965	AD	-	-	-	-	ND	27.0	5.2	tr	14.4	3.6	50.2/49.8	1260	0.453
4-4	1973	WA	-	-	-	-	ND	27.4	5.2	tr	14.8	4.0	51.4/48.6	1260	0.403
4-5	'new'	CGE	-	-	-	-	tr	35.4	13.4	tr	10.0	ND	58.8/41.2	1254	< 0.001
4-6	'new'	W	-	-	-	-	ND	20.2	10.0	tr	ND	ND	30.2/69.8	1254	0.014
4-7	'new'	FP	-	-	-	-	tr	20.8	9.8	tr	tr	ND	30.6/69.4	1254	0.041

Table 6 : Legend

- Samples:

Group 1 (1-1, 1-2, etc.) - variable time-in-service.
Group 2 - 2-1 to 2-4 - CGE Transformers; variable kva/volume ratio
    - 2-5 to 2-6 - FP Transformers; variable kva/volume ratio
Group 3 - variable fluid type - 3-1 and 3-2 Pyranol
    3-3 and 3-4 Chlorextol
    3-5 and 3-6 Inerteen
Group 4 - 4-1 and 4-2 - 'very old' transformers; large variation in kva relative to fluid volume.
    - 4-3 and 4-4 - transformers which had failed in service
        AD - Adelaide Street (Toronto Hydro)
        WA - Walkerton, Ont. (Canada Packers)
    - 4-5, 4-6 and 4-7 - new Pyranol, Inerteen and Chlorextol.

- Manufacturer: (fluid type)			
	CGE	- Canadian General Electric	(Pyranol)
	FP	- Ferranti-Packard	(Chlorextol)
	W	- Westinghouse	(Inerteen)
	AD	- Brown Boveri	(Pyroclor)
	WA	- Foster Electric	(Inerteen)

- 1,3,5-Cl_3Bz - 1,3,5-trichlorobenzene content (± 0.05% w/w)
- 1,2,4-Cl_3Bz - 1,2,4-trichlorobenzene content (± 0.05% w/w)
- 1,2,3-Cl_3Bz - 1,2,3-trichlorobenzene content (± 0.05% w/w)
- 1,2,3,5- & 1,2,4,5-Cl_4Bz - 1,2,3,5- & 1,2,4,5-tetrachlorobenzene content (± 0.05% w/w)
- 1,2,3,4-Cl_4Bz - 1,2,3,4-tetrachlorobenzene content (± 0.05% w/w)
- 1,2,3,4,5-Cl_5Bz - 1,2,3,4,5-pentachlorobenzene content (± 0.05% w/w)
- TCDF (ppm) - concentration of 2,3,7,8-tetrachlorodibenzofuran in askarel (ppm)

the GLC/FID chromatograms of a 'new' Chlorextol and a used (1957) Chlorextol are shown in Figures 7a and 7b respectively.

2.3.2 Analysis of Askarel Samples for PCDF and PCDD

2.3.2.1 Isolation of PCDF/PCDD Fraction

Aroclor 1254, precleaned (i.e. PCDF and PCDD removed) on a florisil column, was spiked with varying amounts of TCDF and then subjected to the fractionation procedure outlined in section 2.2.2.2. In all cases greater than 80% recovery of the TCDF was obtained using this method. Any interference due to large quantities of PCB was also effectively removed usually after one pass through the alumina and florisil columns.

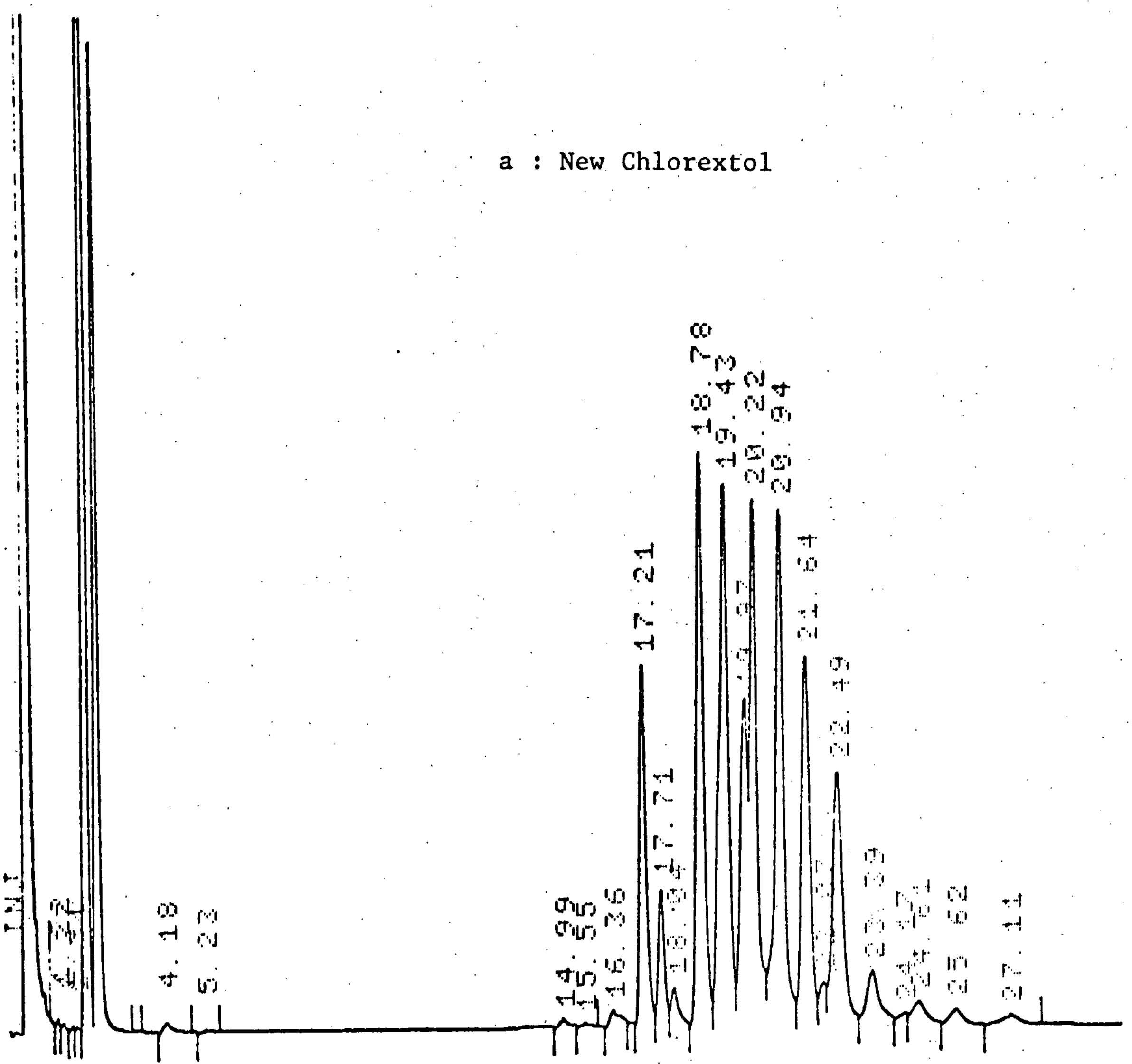
2.3.2.2 GC/MS Analyses of the PCDF/PCDD Fraction

Figure 8 shows the total ion chromatogram of the PCDF/PCDD fraction isolated from an old Aroclor 1254 sample. The major peaks are assigned according to their mass spectra.

It is of some interest that terphenyls and quaterphenyls were detected in this fraction of the PCB mixture. Although not visible as peaks on the total ion chromatogram, penta- and hexachlorodibenzofuran were also detected in this fraction when the GC/MS system was operated in the SIM mode.

Terphenyls and quaterphenyls were identified in most of the PCDF/PCDD fractions analyzed although usually in very small amounts. Tetra-, penta-, and hexachlorodibenzofurans were detected in all of the askarel samples analyzed by GC/MS. In some samples analyzed by GC/MS in the SIM mode, traces of PCDDs were detected but their quantities were usually less than 5% of the individual PCDFs detected. From these initial results it was assumed that these levels of PCDDs were insignificant relative to those of the PCDFs (i.e. < 0.1 ppb total PCDDs).

a : New Chlorextol



b : Old Chlorextol

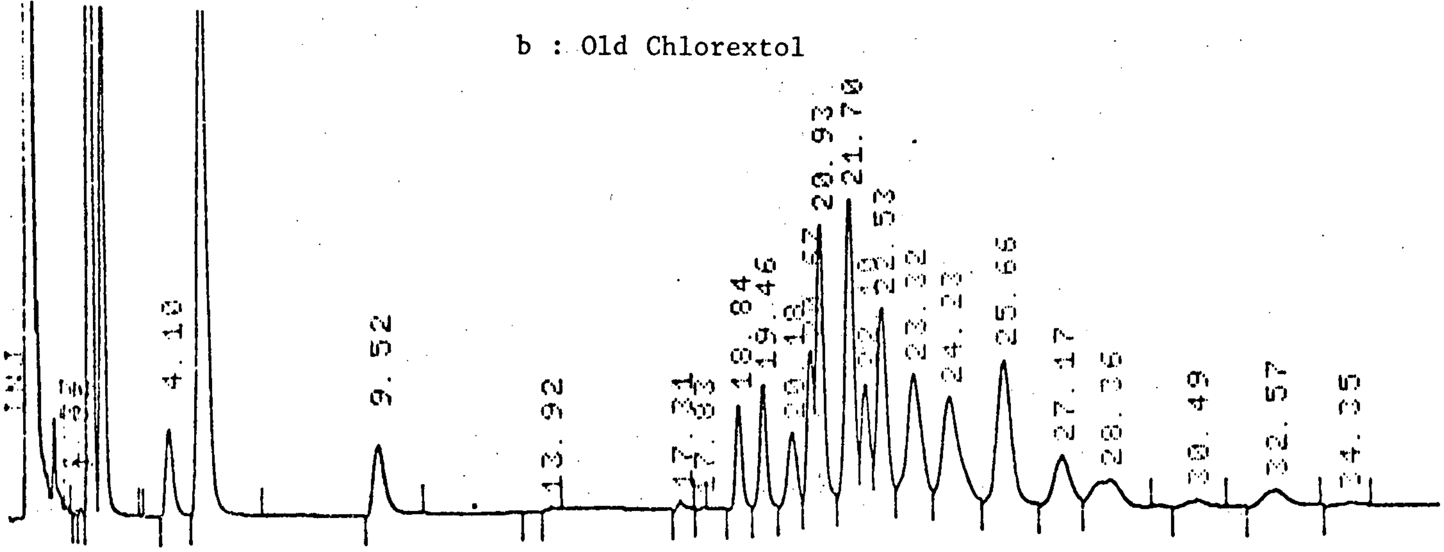
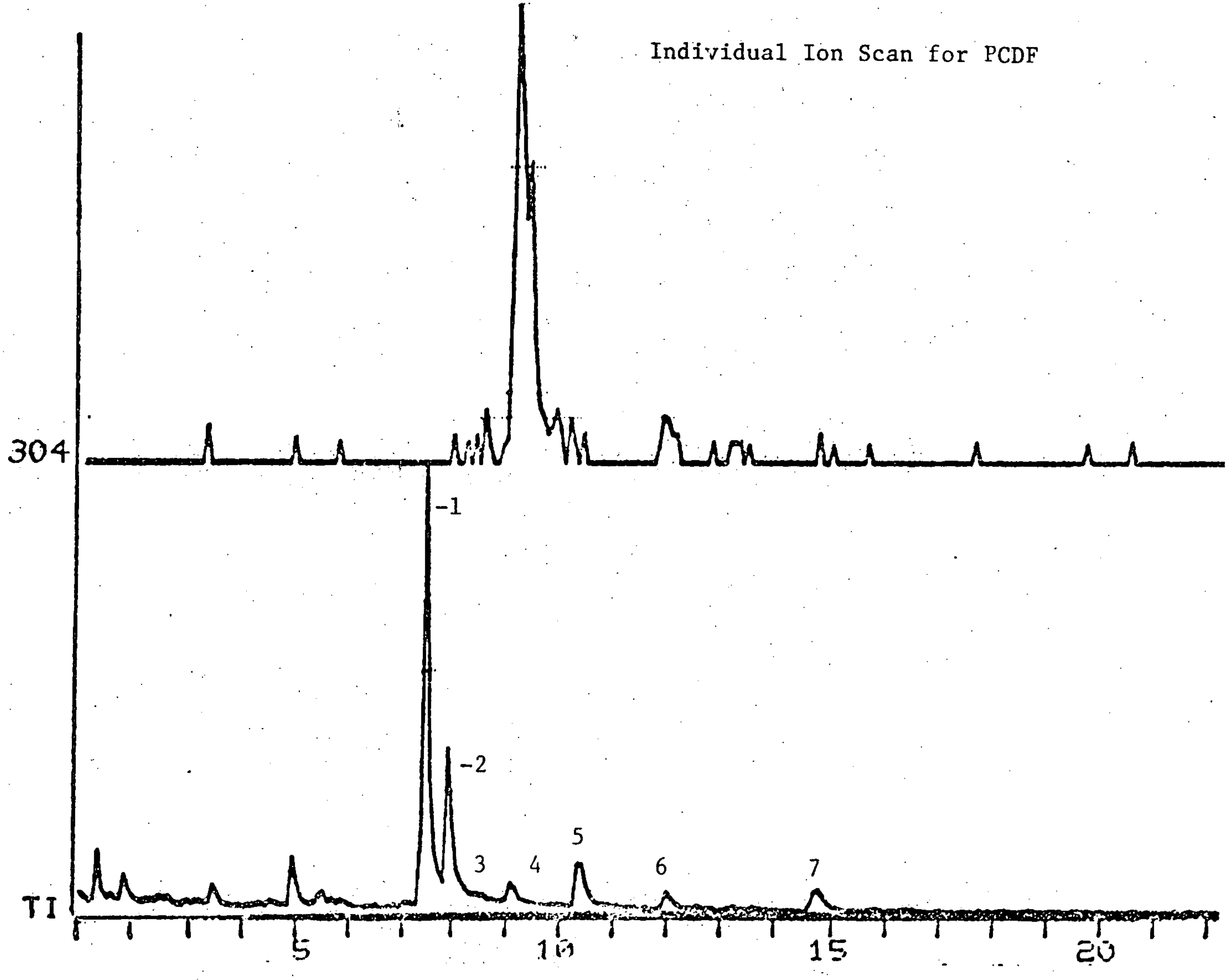


Figure 7 : GLC Analysis of Askarel for Chlorobenzenes and PCB



Peaks Identified : 1. terphenyl
2. terphenyl
3. Cl terphenyl
4. Cl_4 dibenzofuran
5. Cl terphenyl
6. quaterphenyl
7. Cl_6 terphenyl

Figure 8 : GC/MS Analysis of PCDF/PCDD Fraction from Aroclor 1254

In the remaining portions of the project, therefore, the askarel samples were only analyzed for PCDFs.

As an example of the operation and output of the GC/MS system in the SIM mode, that is monitoring for individual ions, the total ion chromatogram and the individual ion scans for tetra-, penta-, and hexachlorodibenzofurans for the PCDF/PCDD fraction taken from a used Chlorextol sample are shown in Figure 9.

2.3.2.3 Perchlorination of the PCDF/PCDD Fraction to Determine Total Dibenzofuran

The perchlorination method as described in section 2.2.2.4.1, was tested for percent recovery using TCDF and dibenzofuran. In all cases the recovery, determined using standard solutions of octachlorodibenzofuran (courtesy of Dr. C. Rappe), was quite low. Even when the conditions and extracting solvent were varied, the percent recovery remained < 30% and was quite variable thus making this method inadequate for quantitation of total PCDF. This method, however, was used in some initial experiments to confirm qualitatively that dibenzofurans were present in the PCDF/PCDD fractions of some askarel and PCB samples. In all the fractions tested in which TCDF was identified by GLC/ECD, octachlorodibenzofuran was formed when these samples were perchlorinated. For example, Figure 10 shows the GLC chromatograms of the products obtained (i.e. octachlorodibenzofuran) when dibenzofuran (0.01 mg) and the PCDD/PCDF fraction from Aroclor 1254 were perchlorinated by this method.

2.3.2.4 Quantitation of 2,3,7,8-Tetrachlorodibenzofuran (TCDF) in Askarel Samples

The amounts of TCDF in ppm detected in the askarel samples are given in Table 6. All the samples were partitioned and analyzed in duplicate and the

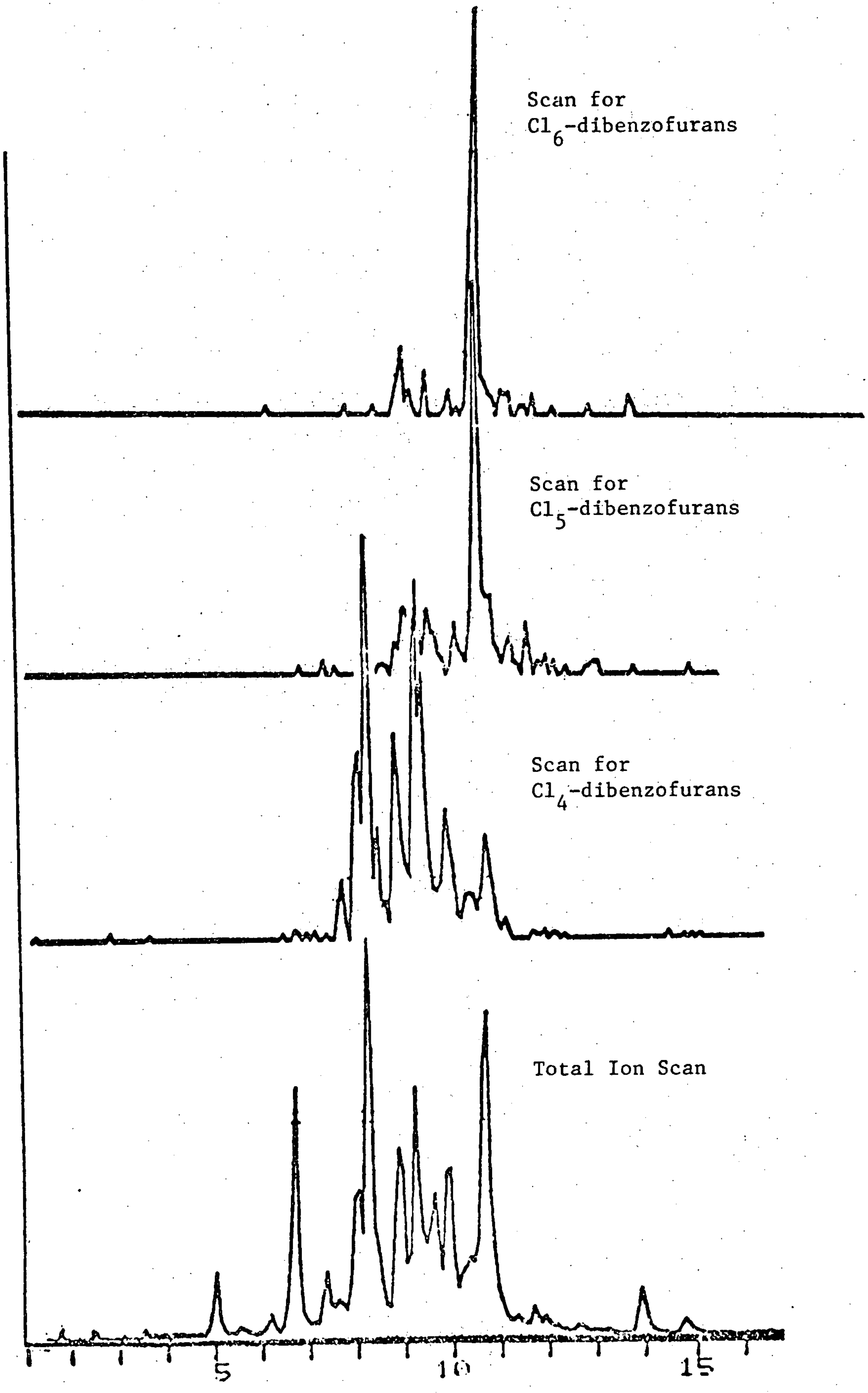


Figure 9 : GC/MS SIM Analysis of PCDF/PCDD Fraction from old Chlorextol

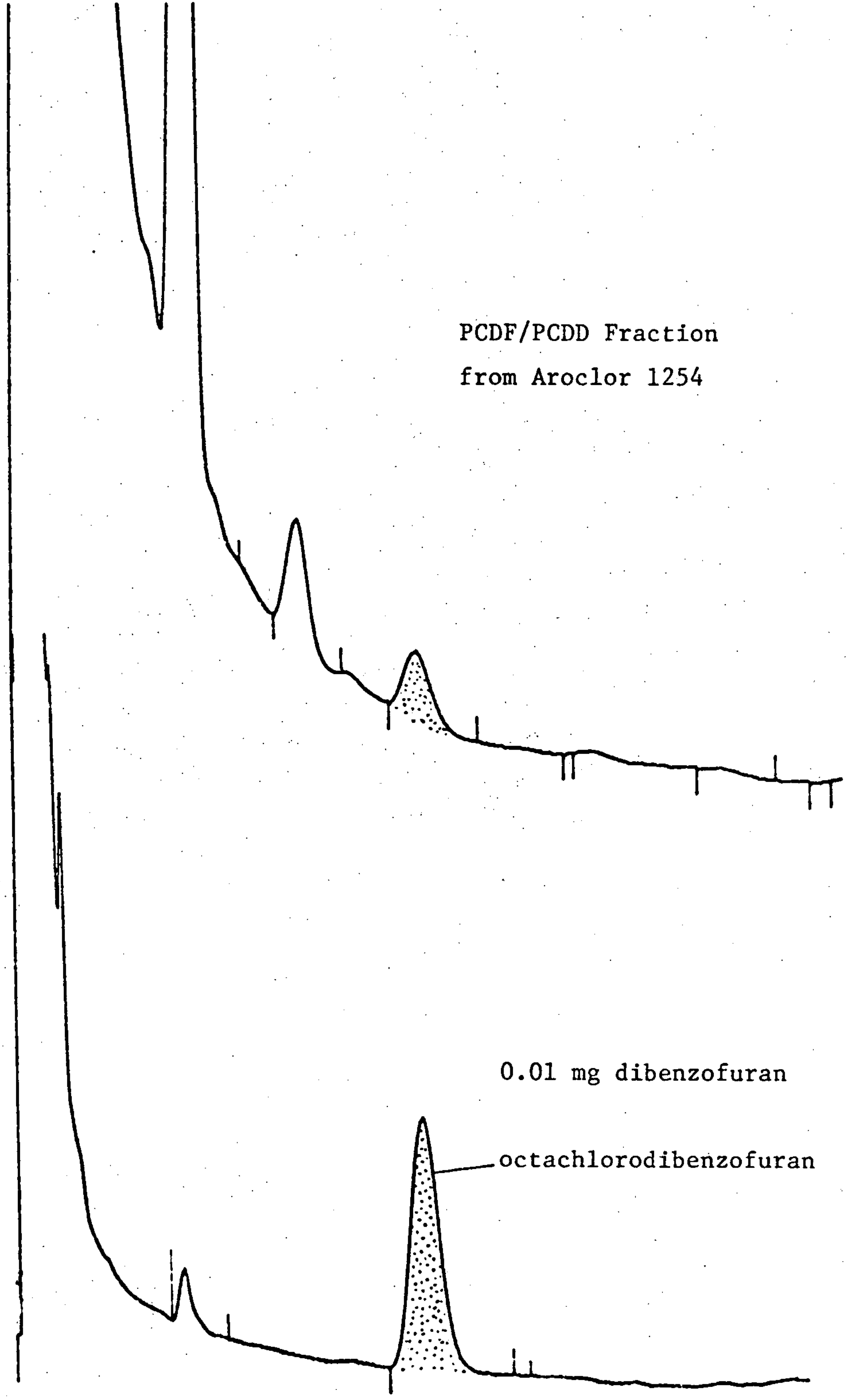


Figure 10 : Perchlorination Products GLC/ECD

results given are the average of the values determined. Generally it was found that the fractionation method and subsequent GLC/ECD analyses were quite reproducible. The GLC/ECD chromatograms of the PCDF/PCDD fractions isolated from Inerteen, Pyranol and Chlorextol used in transformers for ca. 30 years (i.e. since 1947) and the askarel taken from the transformer involved in the Adelaide Street fire are shown in Figure 11.

Group 1 : Time-In-Service

Although the results are somewhat scattered, the level of TCDF in an askarel was found to increase as the time since the transformer was installed increases. It was anticipated that this might be a linear relationship but the data does not allow such a fit to be made. The three askarels taken from 'identical' transformers (1-3, 1-4 and 1-5) showed a marked variation in TCDF levels. This indicates that time-in-service may not be the only variable involved for the transformers samples.

Group 2 : KVA/Volume

For the two sets of transformers (two different manufacturers) where the only variable was the kva/volume ratio, the levels of TCDF showed no observable trend, in fact, they remained reasonably constant in each series. It is possible that even for the highest kva/volume ratio, the liquid volumes are already so large that any increase in fluid volume does not decrease the operating temperature significantly and thus will have little or no effect on formation of PCDFs.

Group 3 ; Manufacturer/Fluid Type

In comparing the three major fluid types (Pyranol, Inerteen and Chlorextol), the levels of TCDF in Chlorextol were lower (ca. 25%) than those

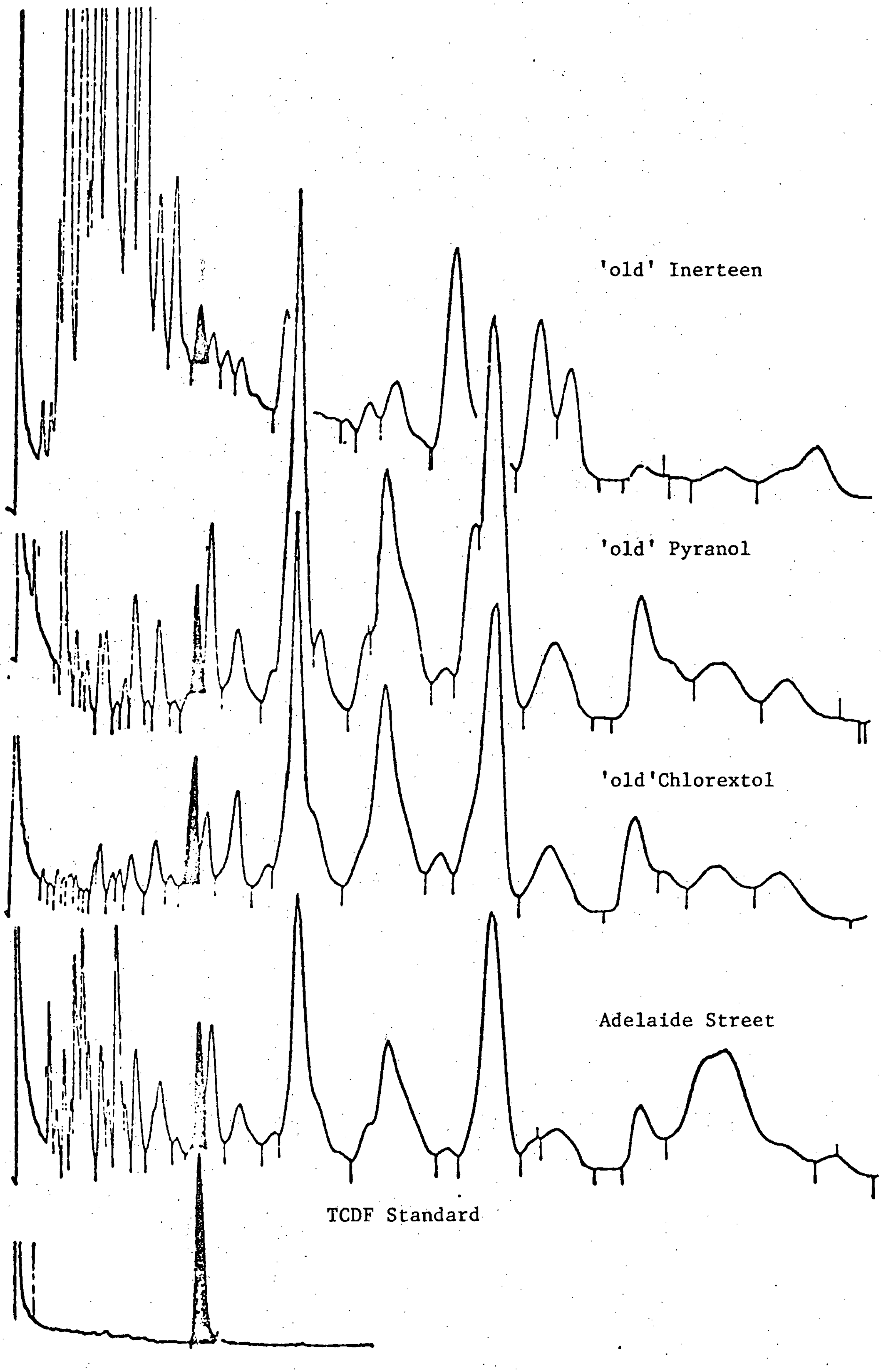


Figure 11 : GLC/ECD of PCDF/PCDD Fractions

in the other two fluids. Whether this is due to the actual fluid or to the construction of the transformer is not known. The three fluids sampled all have essentially the same composition and the transformers should all be of the same basic construction. The lower levels of PCDFs in the Chlorextol filled units may possibly be due to a 'purer' batch of Aroclor in the original fluid, or to lower operating temperatures of these transformers.

Group 4

The two transformer askarels (4-1 and 4-2) sampled from units that had been in service for approximately 30 years, were contaminated with ppm levels of TCDF. The level of TCDF in the askarel from the transformer with the lower kva (kva/volume = 0.08) was more than twice that in the higher kva transformer askarel.

The levels of TCDF in the two transformers which failed while in service were not extremely high relative to the other askarels tested. Short periods of arcing or 'above normal' temperatures may not be enough to induce changes in the askarels. The soot from the Adelaide Street fire did contain high levels of PCDFs compared to the transformer oil, but these were more likely formed when the spilled oil was exposed to the high temperatures of the fire. The PCDFs in the oil itself were probably formed during the normal operation of the transformer.

The final three samples tested in this group were unused Inerteen, Pyranol and Chlorextol. They contained only low levels of TCDF relative to the used oils and represent a 'zero' level. The TCDF found in these oils is most probably formed from the chlorination of a dibenzofuran impurity in the original biphenyl.

2.4 DISCUSSION

Only one of the variables tested in this portion of the project, that being time-in-service, was determined to have an effect on the TCDF levels in askarel; the longer the unit was in service, the higher the concentration of TCDF in the fluid. It was anticipated that this relationship would be linear, but the final data was too scattered to be fitted to a line.

Variations in the kva/volume ratio and the fluid type had no consistent effect on the TCDF levels. In two 'worst case' samples (4-3 and 4-4), where there was an extreme increase in the kva relative to the fluid volume in the transformers, there was a corresponding increase in the TCDF levels. Whether this increase was only due to the kva or kva/volume ratio could not be resolved due to the limited number of samples.

Analysis of the data also suggests that there may be a number of unexpected variables in a transformer and its operation which may all contribute to the formation of PCDFs. For example, sample 2-6 (see Table 6) has a different chlorobenzene (PCBz) content and composition from the other samples in this series, and, at the same time, has a higher TCDF concentration. As previously mentioned, PCBzs, when heated at ca. 600°C in quartz ampoules, yield large amounts of PCDFs[82] and thus the presence of certain PCBz congeners may be responsible for the formation of PCDFs in transformer askarels.

The load under which a transformer is operated is also suspected to be a major factor in the formation of PCDFs. Take, for example, samples 3-1 and 2-1. These transformers are identical in all respects except that 3-1 is in the Central Utilities Plant and 2-1 is in a residence, both at the University of Guelph.

Although accurate records are not available, 3-1 is usually operated under a higher, more continuous load than 2-1, and the askarel taken from 3-1 has a higher TCDF concentration. Unfortunately, due to the unavailability of accurate records, transformer load could not be isolated as a single variable for a sufficiently sized sample group.

The effects of discharging or arcing in a transformer on the levels of PCDFs in the contained askarel appear to be negligible in the two transformers sampled. As previously suggested, these periods of abnormal operation are most likely too short in duration to cause any reactions to occur in the askarel.

It should be pointed out at this time that, although the retention time of the peak in the PCDF/PCDD fraction corresponds to that of TCDF, there may be more than one tetrachlorodibenzofuran isomer involved in this peak (there are 38 tetrachloro isomers possible). GC/MS however, does confirm the presence of tetrachlorodibenzofurans in these fractions.

*NB may not be 2,3,7,8 isomer

In summary, significant levels of PCDFs are formed in askarel filled transformers during their normal operation. The detection of these compounds as contaminants in PCB-based fluids currently in use even more necessitates strict controls on the use of PCBs and the 'complete' destruction of these fluids when they do come out of service.

3 INCINERATION/TRAPPING EXPERIMENTS USING AROCLORS AND ASKARELS

3.1 INTRODUCTION

Laboratory scale pyrolyses of individual PCB congeners and commercial mixtures, as previously mentioned, has been found to yield significant quantities of PCDFs[37,41,46,47]. To our knowledge there have been no reports as to the products formed when askarels (i.e. chlorobenzene/PCB mixtures) are pyrolyzed.

In the following phase of this project, the incineration of PCBs and askarels is simulated using a laboratory scale pyrolysis unit, and the formation of PCDFs and PCDDs investigated.

3.2 EXPERIMENTAL

3.2.1 PCBs and Askarels used for Pyrolysis

Two PCB mixtures, Aroclor 1254 and Aroclor 1016, and three askarels, Chlorextol, Pyranol and Inerteen, were obtained during the sampling carried out for Section 2. These mixtures were then purified (i.e. PCDF/PCDD fraction removed) using the method described in Section 3.2.3.1 prior to using them for the pyrolysis experiments.

3.2.2 Pyrolysis of PCBs and Askarels

3.2.2.1 Apparatus

The pyrolysis unit consisted basically of two ovens, a movable flash heating oven and a fixed reaction oven, surrounding a quartz tube (20 cm. x 0.4 cm i.d.) as shown in Figure 12. Compressed air (technical), filtered through sulfuric acid on silica gel (20% w/w) and activated charcoal, was fed into the sample at 200 ml/min at a pressure of 6 atmospheres. The products of incineration were collected at two points; at the end of the quartz tube, Q, and in a cold trap connected to the end of the tube, C.

3.2.2.2 Procedure

The PCB or askarel, dissolved in hexane, was deposited on glass wool in the reaction tube (see Figure 12). The weights of PCB or askarel used in the pyrolyses are given in Table 7. The hexane was allowed to evaporate with no air flow prior to switching on the ovens.

The fixed and movable ovens were then set to operate at ca. 500°C and ca. 650°C respectively. Once both ovens had reached these temperatures, the air flow was started, dry ice/ethanol cold traps were set in place, and the movable oven was positioned around the portion of the quartz tube containing the glass wool and the PCB. After 3 minutes, the ovens were switched off and the cold trap and reaction tube were removed. The products at Q and C were then collected for analysis by dissolving them in hexane.

3.2.3 Analysis of Pyrolysis Products

3.2.3.1 Isolation of PCDF/PCDD Fraction

The hexane solutions of the pyrolysis products were first concentrated to ca. 0.5 ml. This concentrate was then quantitatively transferred to the top of a microcolumn packed with sulfuric acid on silica gel (20% by weight) and then eluted with hexane (6 ml). This eluate was then again concentrated to ca. 0.5 ml and then applied to the top of a micro alumina column (basic alumina; 1 g.). This column was then eluted, first with 2% methylene chloride in hexane (10 ml), to remove chlorobenzenes and PCBs, and then with 50% methylene chloride in hexane (10 ml.), to elute the dioxin and furan products. The second eluate was evaporated just to dryness and then reconstituted with toluene containing 2,5-dichloro-4'-methylbiphenyl (5 mg/ml) as an internal standard. This solution was then analyzed and quantitated by GC/MS in the SIM

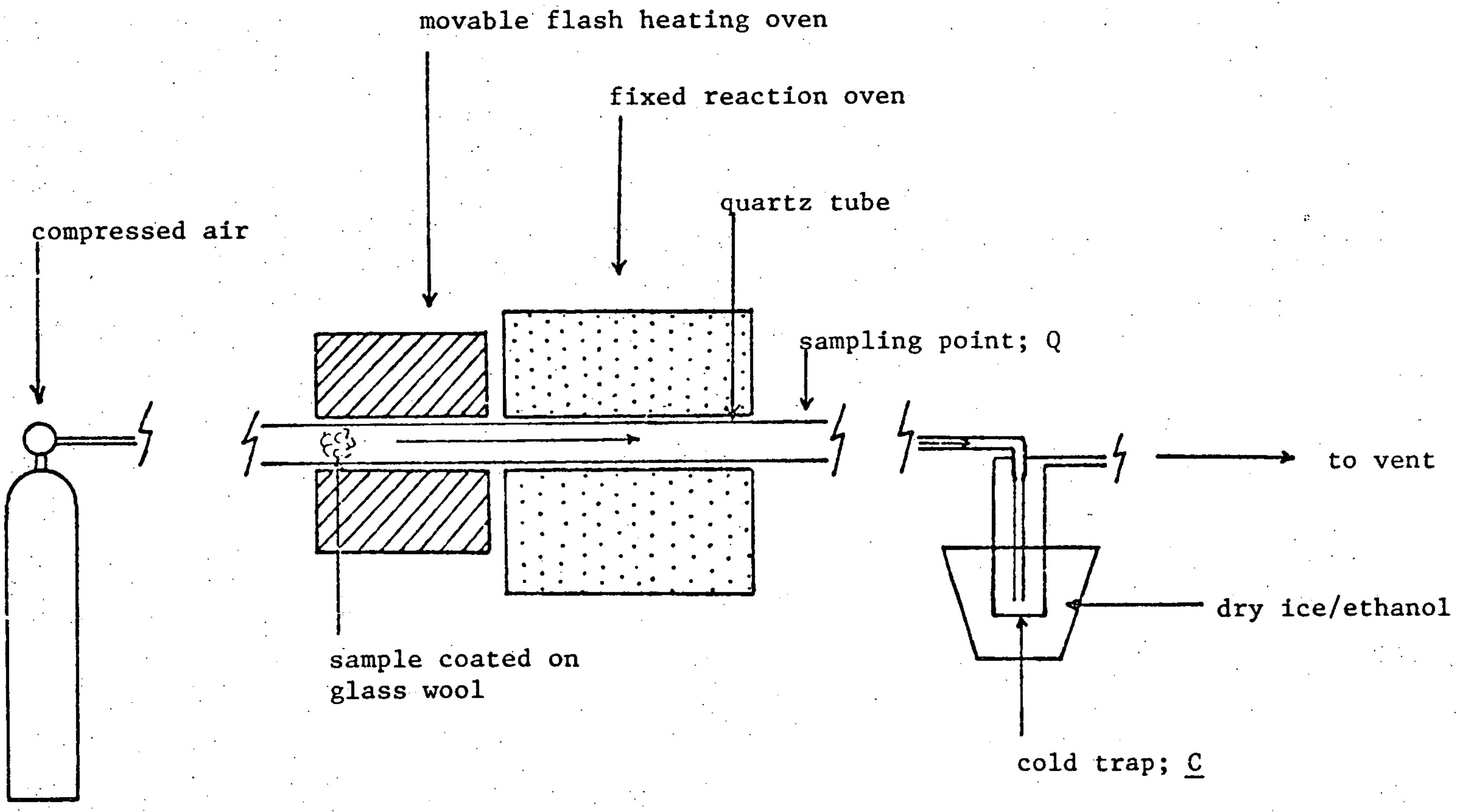


Figure 12 : Incineration/Trapping Apparatus for Pyrolysis of PCBs

Table 7 : Pyrolysis of PCBs and Askarels

			Weight of Tetrachlorodibenzofurans Formed			
PCB or Askarel	Weight Pyrolyzed (mg)	Position of Sample	Actual Weight (µg)	Per Gram of Starting Material (µg/g)	Total (Q+C)	Average of Both Runs (µg/g)
Aroclor 1254	25.0	Q	2.20	88.0		169.3
		C	1.33	53.2	141.2	
	40.0	Q	4.90	122.5		
		C	3.03	75.8	197.3	
Aroclor 1016	25.0	Q	0.038	1.52		2.53
		C	0.027	1.08	2.60	
	40.0	Q	0.072	1.80		
		C	0.026	0.65	2.45	
Pyranol	25.0	Q	0.53	21.2		NA
		C	0.53	21.2	42.4	
	0.25	Q	0.048	191.7		
		C	0.074	297.0	488.8	
Inerteen	0.25	Q	0.030	118.3		193.1
		C	0.030	121.9	240.2	
	0.25	Q	0.033	133.7		
		C	0.003	12.2	145.9	
Chlorextol	0.25	Q	0.023	93.5		221.1
		C	0.025	100.2	193.7	
	0.25	Q	0.021	82.8		
		C	0.041	165.7	248.5	

mode. To continually check the response of the GC/MS, repeated injections were made of a standard solution containing the internal standard, 1,2,3,4-tetrachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin (all 5 mg/ml in toluene).

3.3 RESULTS

The results of the incineration/trapping experiments are summarized in Table 7. The amounts of tetrachlorodibenzofuran formed are reported as μg/gm of starting material.

Analyses of the 'cleaned-up' starting materials prior to pyrolysis showed no PCDFs or PCDDs. GC/MS analysis of the pyrolysis products revealed that only PCDFs are formed when PCBs or askarels are pyrolyzed. No PCDDs or other compounds such as terphenyls or quaterphenyls were detected by GC/MS. A typical GC/MS - SIM for the pyrolysis products of an askarel is shown, in Figure 13.

The pyrolysis experiments for only one temperature (~500°C) are reported. Preliminary experiments at ~100°C gave no detectable change in the starting material within the 3 minute reaction time.

3.4 DISCUSSION

The formation of PCDFs when PCBs or askarels are incinerated is consistent with past research. Their formation at temperatures of ca. 500°C indicates that for 'safe' incineration of PCBs, temperatures of at least 700°C are necessary (> 1000°C preferably).

The absences of any other contaminants, such as terphenyls and quaterphenyls, in the pyrolysis products suggests that their presence in Aroclors or askarels is most likely due to contamination of the original biphenyl. They do not form under pyrolytic conditions. It is also interesting to note that Aroclor 1016 gave significantly less PCDF than Aroclor 1254 when incinerated. These

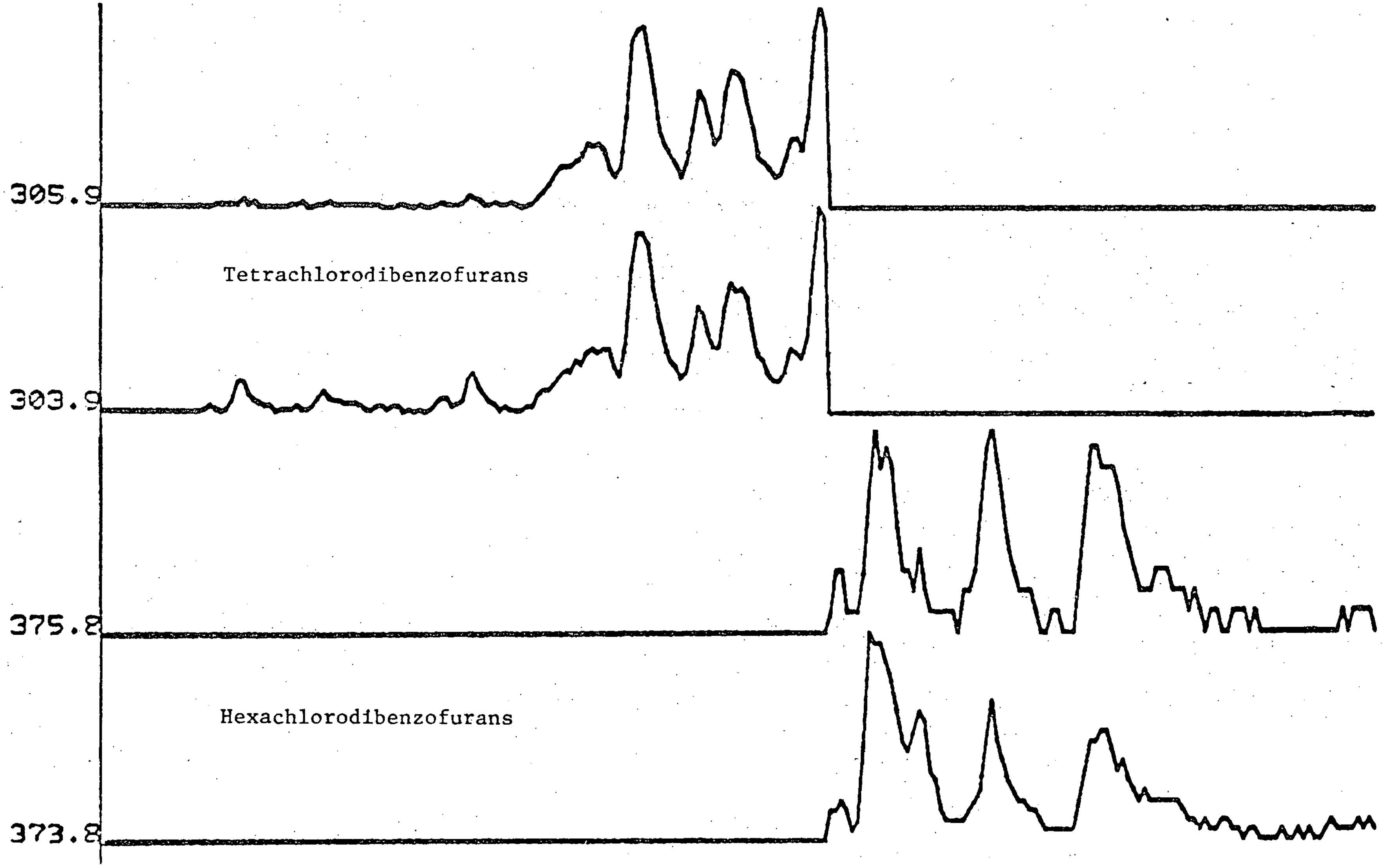


Figure 13 : Individual Ion Scans (SIM GC/MS) for Tetrachloro- and Hexachlorodibenzofurans in PCDF/PCDD Fraction of Pyrolyzed Pyranol

lower levels are to be expected since 1016 is of lower chlorine content and therefore does not contain as much of the higher chlorinated biphenyls (i.e. pentachloro- or hexachloro-) which are necessary precursors of tetrachlorodibenzofurans.

In summary, the formation of PCDFs when askarels are exposed to sufficient oxygen and high temperatures demonstrates that fires associated with PCB-filled transformers are potentially hazardous and that any situations where PCBs may be pyrolyzed should be handled with extreme caution.

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APPENDIX A

TRANSFORMERS (POWER TYPE) : BASIC THEORY, CONSTRUCTION AND USE

1 INTRODUCTION

The generation, transmission and distribution of electric power is achieved by using what are called three-phase power systems consisting of three-phase generators, transformers and transmission lines. These systems are more economical than single-phase systems when large amounts of electrical energy have to be generated and distributed.

It is not very practical to generate electricity at large voltages, but it is practical to transmit power over large distances at high voltages since voltage drops as the distance from the source increases. Transformers are, therefore, used at generating stations to step up the generated voltages to transmission levels. A common value for a generated voltage is 13,800 volts, while transmission voltages can be as high as 220,000 volts. Once the electric power reaches the distribution points the voltages are decreased, using step-down transformers, to a level suitable for domestic and industrial use.

A typical power system is shown in Figure 1. Step-up, power transformers are primarily located at generating stations where the step-down type are at the substation and distribution installations. Brief discussions of transformer theory and construction are given in the following sections. For more detailed information, the references given should be consulted.

2 Theory of Transformer Operation

A transformer is described as an electric device without continuously moving parts which, by electromagnetic induction, transfers energy from one

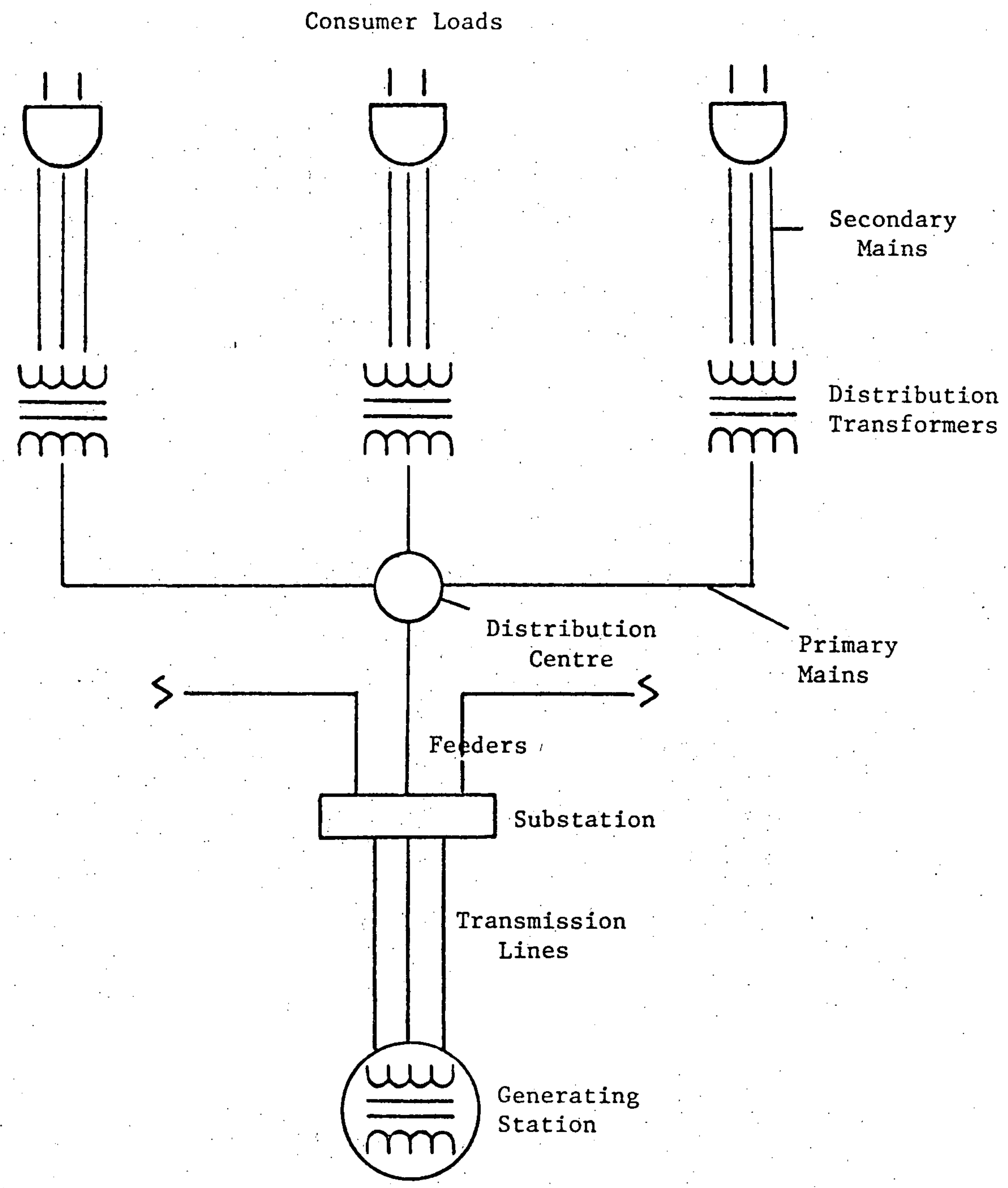


Figure 1 : A Typical Power Distribution System

circuit to another. A simple two coil transformer is represented in Figure 2.

The two coils, Winding A and Winding B, are inductively coupled through a ferromagnetic ring called the iron core. Any magnetic flux (ϕ) passing through coil A will also pass through coil B, that is, the two coils have a magnetic circuit common to both. If the current across a, b changes, the mutual flux across both coils changes accordingly and induces a change in the current in coil B and likewise a change in the voltage across c, d. This induced voltage change in the secondary coil (B) is called the transformer voltage while the action that creates this change in potential difference is known as transformer action.

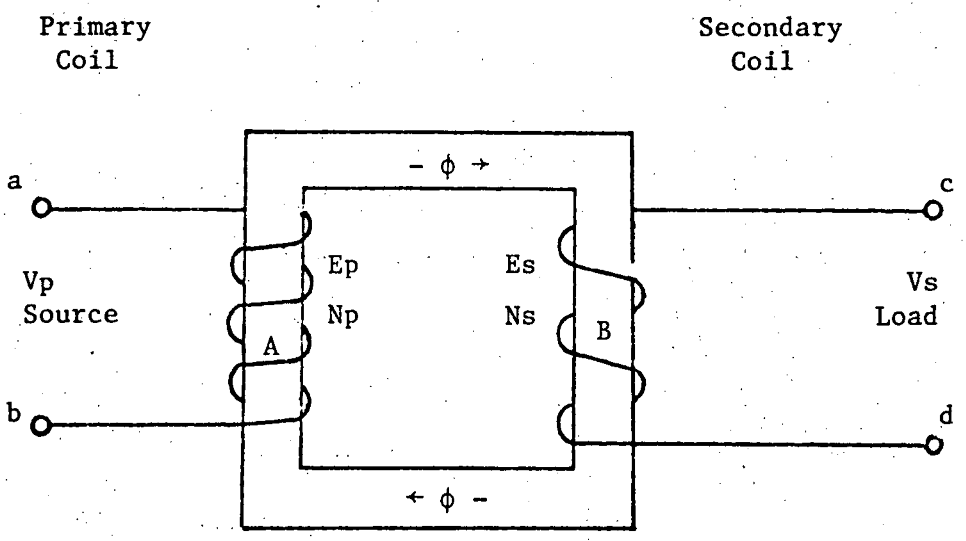


Figure 2: Two Coil Transformer

Most electrical equipment makes use of alternating current (AC) which, in the case of a transformer, would be applied across a, b (see Figure 2). The current in coil A thus changes in magnitude and direction (sinusoidal) which then causes the flux in the core to vary in a similar fashion. The induced voltage in the secondary coil (B) is thus also a sine wave but lagging the applied voltage by 90°, that is, AC current is produced in coil B.

If assumptions are made regarding the various construction features of transformers such as no coil resistance, zero iron loss and a linear magnetization curve, the maximum voltage in coil B is determined by the applied voltage across a, b. This voltage induced in coil B by transformer action is produced by the same flux that crosses coil A. In an ideal transformer, the ratio of the induced primary voltage (Ep) in coil A to the secondary induced voltage (Es) in coil B is the same as the ratio of the number of primary turns to the number of secondary turns (Np/Ns). Assuming very little resistance in the windings, the induced primary voltage (Ep) will equal the applied primary voltage (Vp) across a, b. With the same assumption, a (Vs) similar relation would exist for the secondary induced (Es) and applied voltages and the following relation would exist,

$$Np/_{Ns} = Ep/_{Es} = Vp/_{Vs} = a \qquad (1)$$

where "a" is called the transformer ratio. If Vs is less than Vp (i.e. a>1) the transformer is termed a step-down type. Conversely, if Vs is greater than Vp (i.e. a<1) the unit is called a step-up transformer.

3 Three-Phase Transformers

In the past, when large voltages were to be reduced, a series of three similar transformers were connected together to supply, what is termed, three-phase service. There are four standard ways to connect three single transformers together to supply this type of service. These four arrangements are termed Y-Y, Δ-Δ, Δ-Y and Y-Δ. As an example, Figure 3 is a diagram of a common Δ-Y (delta-wye) arrangement for a three-phase transformer system (step-down).

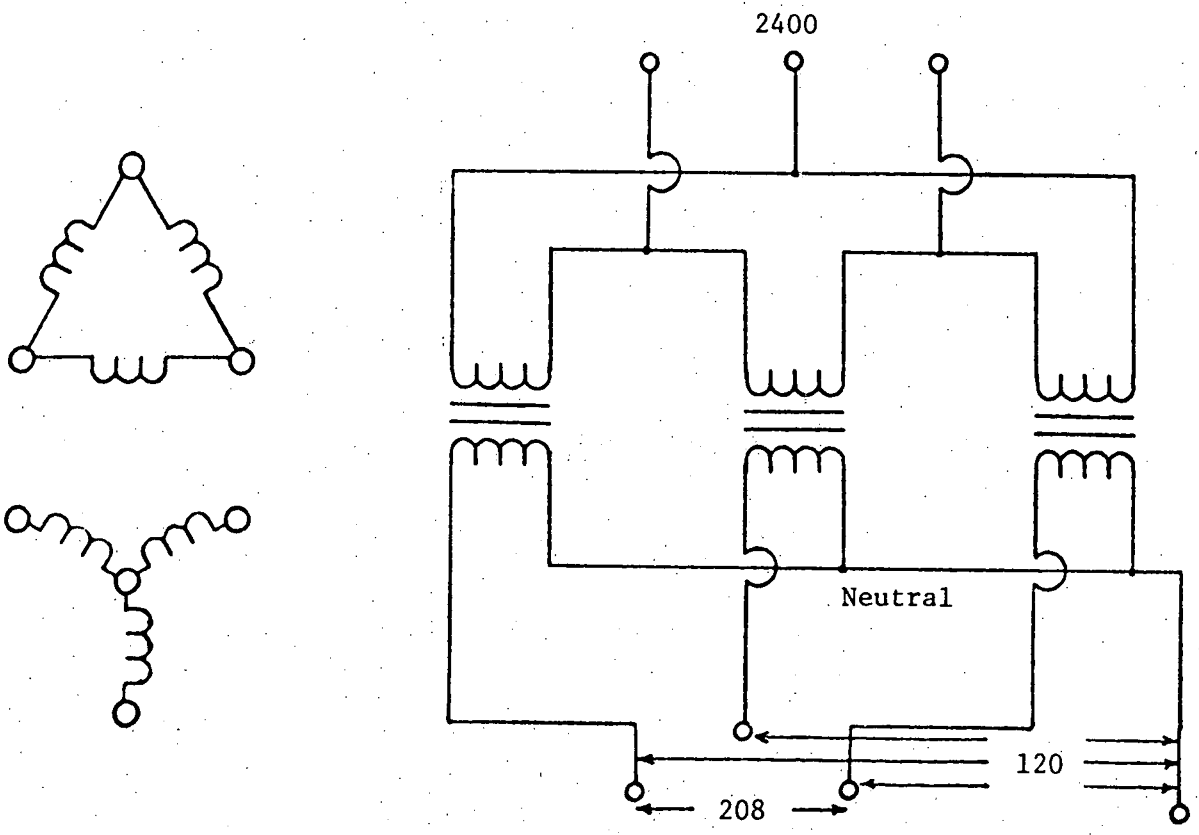


Figure 3 : Δ-Y Three-Phase Transformer System

This type of connection (Figure 3) is useful because the secondary voltages can be used to either supply three-phase power equipment (208) or lower voltage equipment such as lights (120).

A schematic representation for the Δ-Y connection is shown in Figure 4. The common primary and secondary voltages for a power transformer are 13,800 and 600 volts respectively. This is a transformer ratio of 23/1 (i.e. step-down). In the delta (Δ) arrangement on the primary side the voltage obtained between any two lines is 13,800 volts (i.e. $V_{AB} = V_{AC} = V_{BC} = 13,800$). The Y (wye) arrangement on the secondary side is shown with a ground to the neutral and the line voltages are 600 volts (i.e. $V_{DE} = V_{DF} = V_{EF} = 600$).

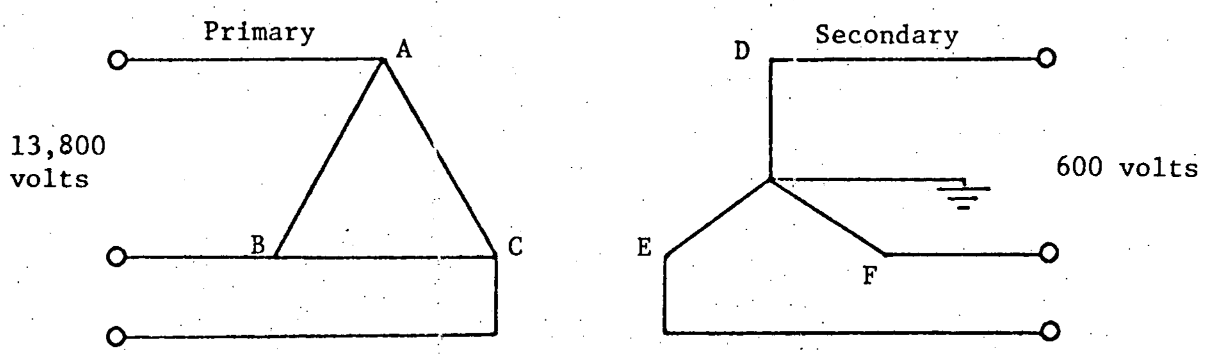


Figure 4: Schematic of Δ-Y 3-Phase System

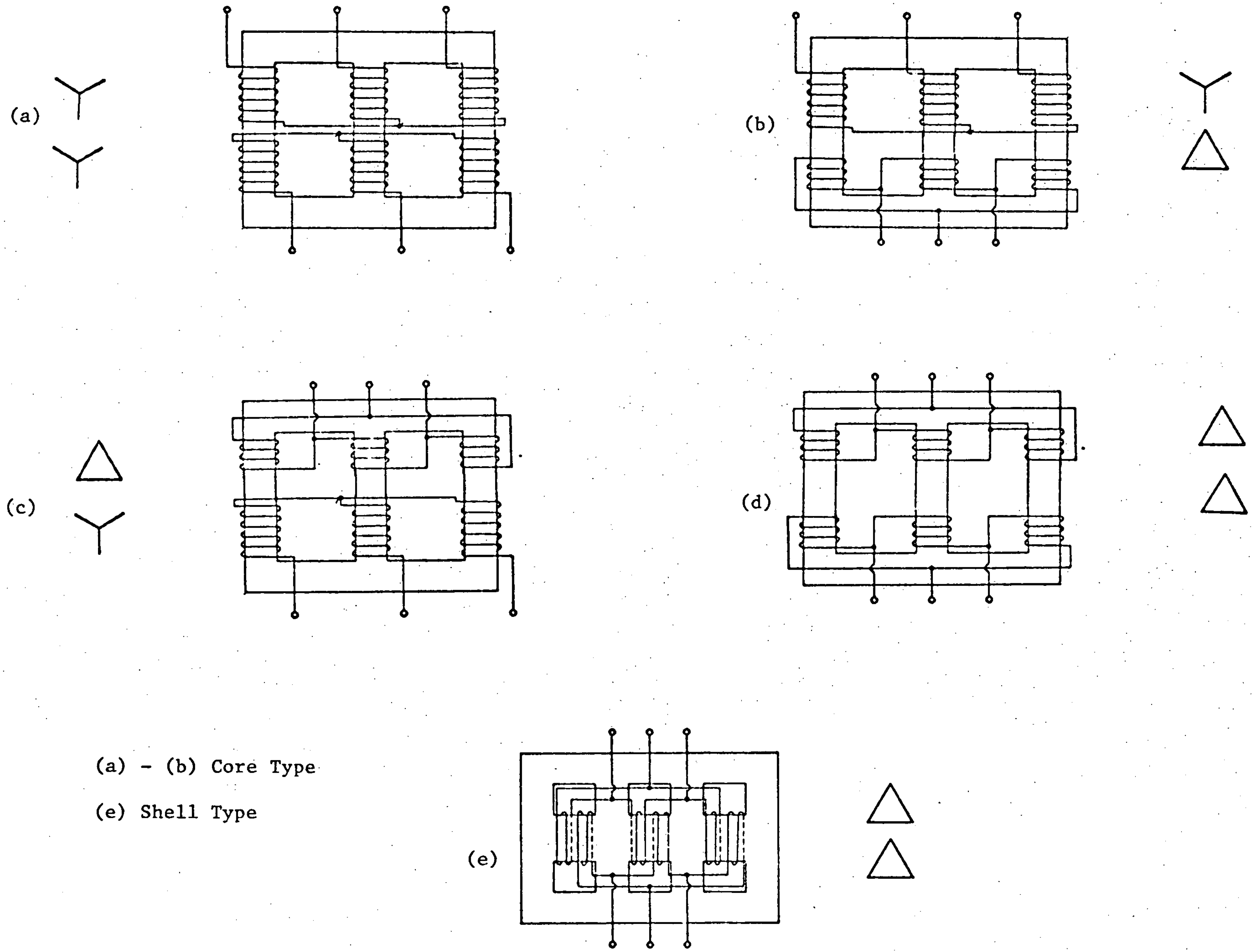
Another voltage, 347 volts, can be obtained from the Y side by connecting any one of the three lines to the ground. In the earlier example (Figure 3) voltages of 208 and 120 were obtained this way.

Compared to three single-phase transformers (i.e. to make up a three-phase system), it is more economical to construct a single three-phase transformer. A three-phase transformer makes use of only one core and thus saves a great deal of iron, copper wire (used in windings) and insulating fluid. These individual three-phase units may be wired internally to give the Δ-Δ, Δ-Y, Y-Δ or Y,Y configurations (Figure 5).

4 CONSTRUCTION

4.1 Iron Core Transformers

Most common power transformers use a ferromagnetic or iron core. There are two types of iron core transformers, core and shell type, which vary basically in the arrangement of the windings on the core. How the coils are arranged in these two types of transformers is depicted in Figure 6. This figure also shows how the successive layers of laminations are assembled in



(a) - (b) Core Type

(e) Shell Type

Figure 5 : Three-Phase Transformer Wiring

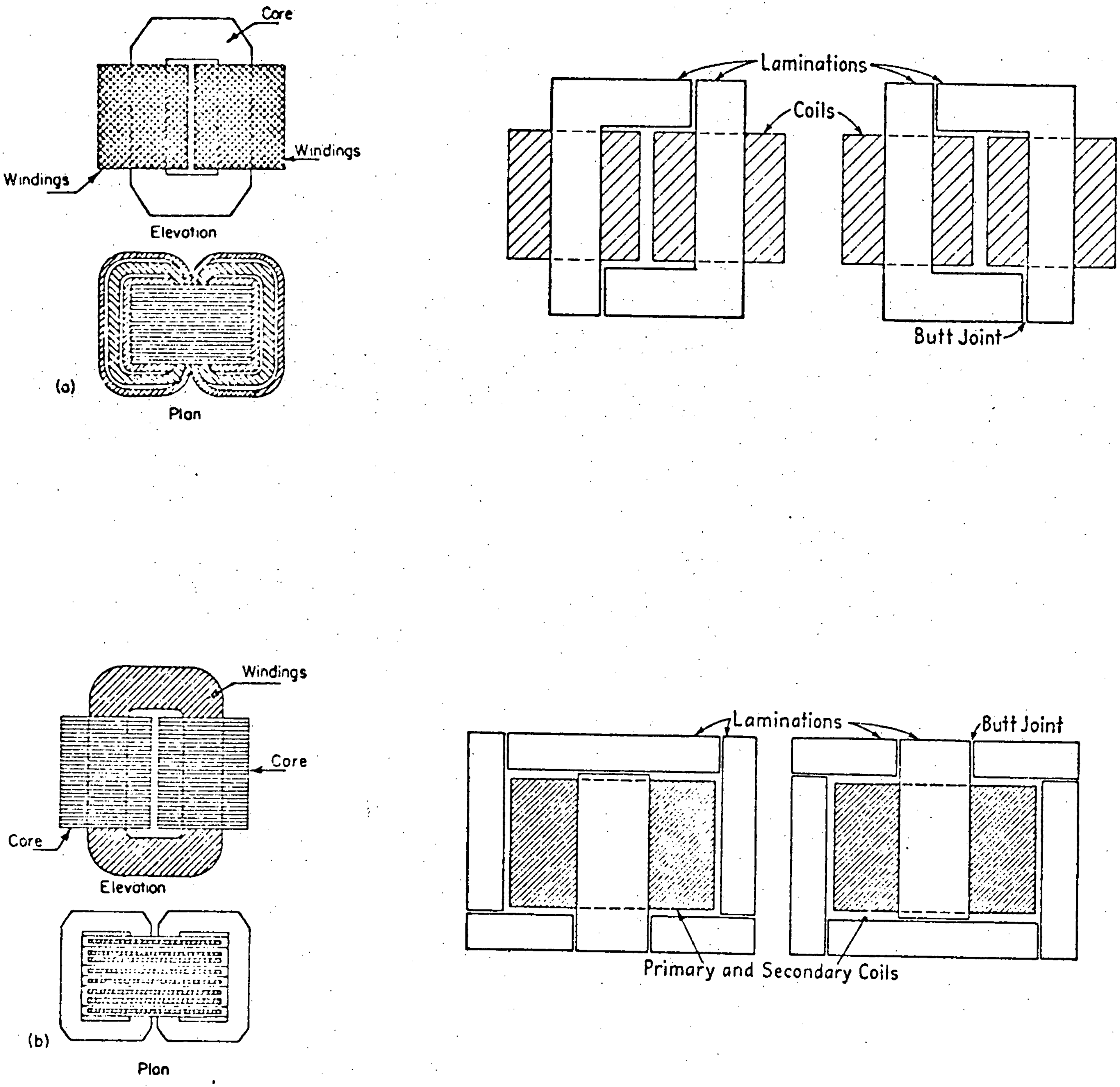


Figure 6 : Core Type, (a), and Shell Type, (b), Transformers Showing Laminations

both types.

In the core type, the primary and secondary coils surround most of the core with each of these coils wrapped around a separate leg of the core. In the shell type transformer, the situation is reversed with the core surrounding the coils.

4.2 Windings

In three-phase transformers, the primary and secondary windings are situated around the core as shown in Figure 5, which also shows the various connections used. As stated earlier, transformer action exists when a mutual flux is present between the primary and secondary coils. The isolation of the individual windings, as depicted in Figure 5, minimizes any flux leakage while at the same time ensuring this mutual flux. This leakage flux is further decreased by having the primary and secondary coils interleaved. This arrangement also optimizes transformer action and decreases the voltage per coil which in turn extends the life of the transformer.

In the coils of three-phase transformers, the early windings are often spaced further apart than the others because under normal conditions the effect of stress voltages are more pronounced in the early part of the coil.

4.3 Insulating Fluids

4.3.1 Composition

The main insulating fluids used in present-day transformers are mineral oils, silicone oils and askarels. 'Askarel' is the generic name for a series of synthetic liquids which have been used in transformers and capacitors for over forty years. These liquids provided a non-flammable, non-oxidizing, insulating and heat transfer medium for use in this equipment operated at power frequencies. There are two general grades of askarel fluids; transformer askarel (Aroclor 1242, 1254 or 1260 and chlorinated benzenes) and capacitor askarel (Aroclor 1016).

Transformer askarels were first introduced in 1932 by the General Electric Company and marketed under their trade name Pyranol, which was essentially a blend of Aroclor 1260 (60%) and trichlorobenzenes (40%). Westinghouse and Ferranti Packard also later introduced their own askarels, Inerteen and Chlorextol, which were of the same composition. In the early 1970's, Aroclor 1254 was substituted for Aroclor 1260 in most askarel mixtures. Also around this time, the compositions of Inerteen and Chlorextol were changed to a 70% PCB : 30% chlorobenzene mixture while Pyranol retained the same basic composition.

In the late 1940's most transformer manufacturing companiesbegan adding what are termed scavengers to their askarels. The first scavenger used was tetraphenyl tin which was added at a concentration of ca. 0.125%. However, at very low temperatures it had a tendency to crystallize out of solution and float on top of the askarel. Because of this solubility problem, Westinghouse later introduced phenoxy-propene oxide as a substitute for tetraphenyl tin.

These scavengers were added to transformer askarels to trap gases that are given off when arcing occurs in a transformer. The major gas formed during arcing is HCl gas, which is very corrosive to the internal components of a transformer. The scavengers react with this gas to neutralize it and prevent any corrosion inside the transformer.

4.3.2 Dielectric Strength

The most important characteristic of any askarel, from the stand-point of transformer operation, is its dielectric strength. The dielectric strength is a direct measure of the askarel's ability to withstand electrical stress without failure. New askarel has a minimum dielectric strength of 35 KV and a maximum water content of 30 ppm. Dissolved water has a significant effect on the insulating capacity of askarel and other transformer oils. The graph in Figure 7 shows the effect of water content, in askarel and mineral oil, on the dielectric strength.

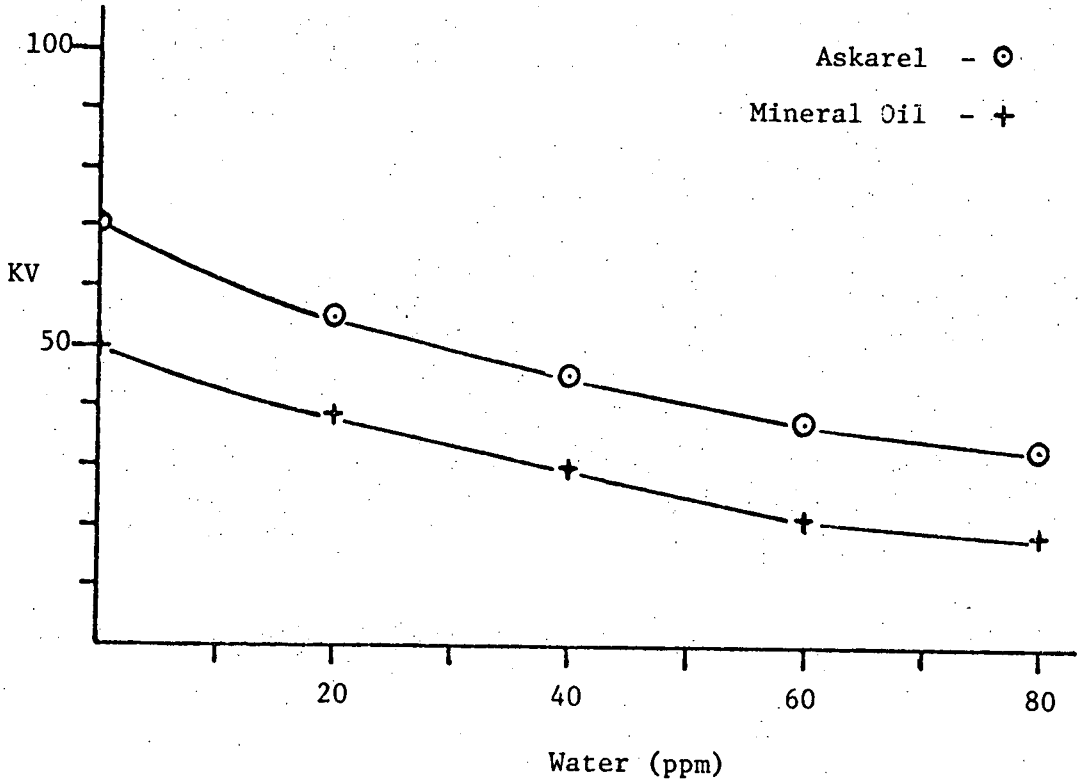


Figure 7 : Dielectric Strength (KV) vs. Water Content (H_2O, ppm).

Transformer manufacturers advise that the water level in an askarel should always be lower than 70 ppm to insure optimum insulation. They also advise that if the dielectric strength drops below 22 KV, and water is present, it should be removed.

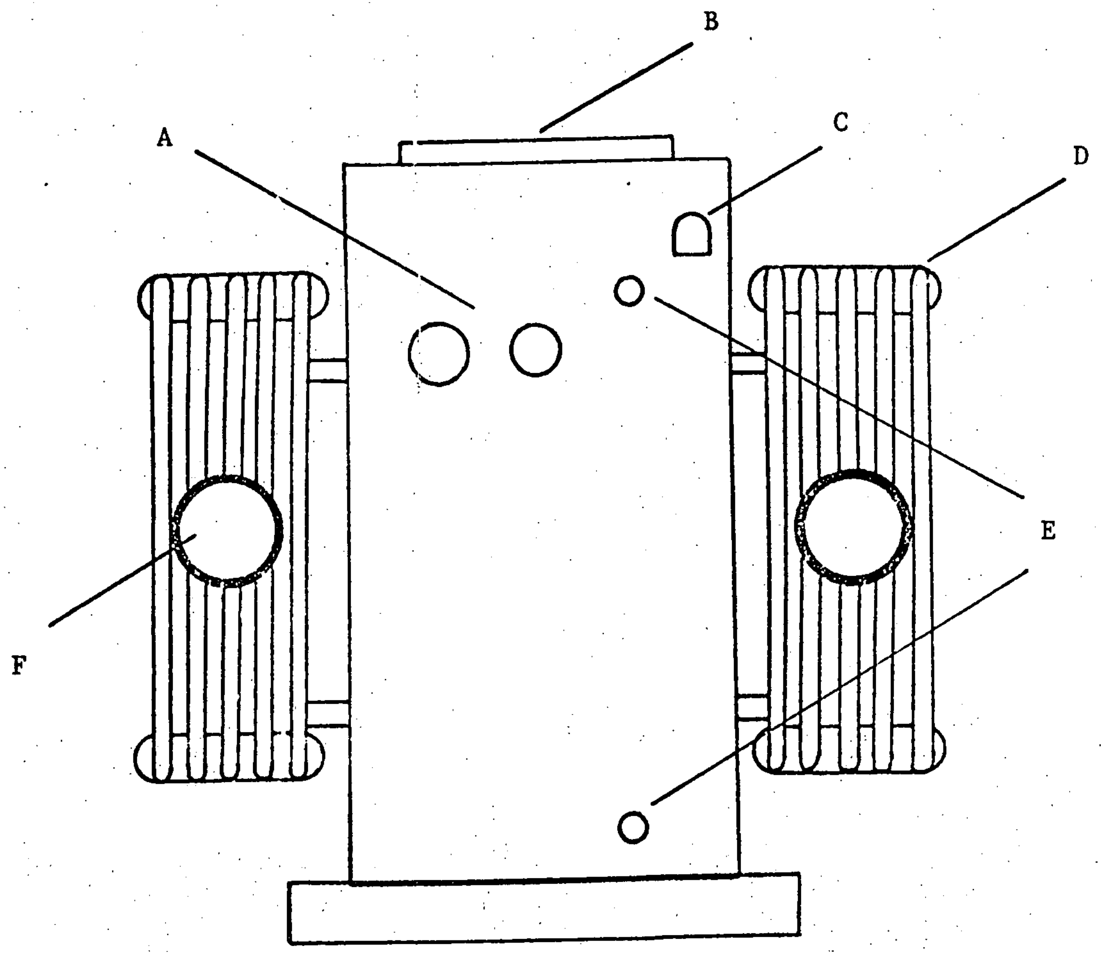
The dielectric strength is also a good indicator of contamination by particulate matter, or dissolved contaminants such as decomposition products resulting from arcing or abnormal operating conditions. For example, a dark askarel having a dielectric strength less than 22 KV most likely contains a large amount of particulate carbon due to repeated arcing.

4.4 Transformer Tank

The winding and core of a transformer are usually enclosed in a reinforced steel tank that is permanently sealed except for the service and maintenance ports. These tanks are very heavily constructed to minimize vibration and noise. Most power transformers are constructed in such a way that external cooling radiators can be added. These radiators are usually forced-air cooled by fans and when they are installed on self-cooled transformers, they allow such a unit to be operated at 115 to 130% of the self-cooled kva rating (see Figure 8).

5 OPERATING TEMPERATURE

Transformers possess self induction as well as mutual induction between individual windings on the core. These characteristics, along with the fact that any electric current flowing in a coil of wire is subject to resistance, will cause a transformer to produce heat when operating. Transformers are usually constructed to operate safely at a maximum temperature rise of 65°C above ambient temperature. The ambient temperature itself should not exceed 40°C so that the maximum operating temperature of any transformer is usually less than 105°C.



A - Temperature and Pressure Gauges
B - Cover Plate
C - Pressure Vent
D - Cooling Radiators
E - Sampling Valves
F - Cooling Fan

Figure 8 : Forced-Air Cooled Transformer

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APPENDIX B: TERMS OF REFERENCE

CHLORINATED DIBENZOFURANS AND DIBENZO-P-DIOXINS: DETECTION AND QUANTITATION IN ELECTRICAL EQUIPMENT AND THEIR FORMATION DURING THE INCINERATION OF PCBs.

PROJECT PROPOSAL

This project is a combination of two related projects concerning the detection and quantitation of the potentially toxic polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD). The two primary topics will focus on;

1) the detection and quantitation of residual PCDF and PCDD in new and used PCB-based transformer oils and
2) the detection and quantitation of PCDF (and PCDD) formed during the incineration of PCB.

The approaches to the two related projects will be considered together in an integrated fashion in phases.

Phase 1

The first phase will involve a detailed background description of PCDF and PCDD with emphasis on the following proposal-related topics.

1) A brief discussion of the chemical, physical and spectral properties of the known PCDF and PCDD isomers.
2) A brief summary of the biological and toxicological properties with an emphasis on those isomer(s) which are toxic.
3) A review of the literature concerning the presence and formation of PCDF and PCDD in commercial PCB-containing electrical fluids and their formation during the incineration of PCB, chlorinated organics and waste material.

Phase II

In discussions with Ontario Hydro personnel arrangements will be made to sample PCB-containing electrical fluids (transformers and capacitors). The study will attempt to select fluids with respect to a number of possible variables which include;

1) the type of PCB-containing fluid (i.e. PCB/chlorinated benzene ratio),
2) the length of time in service (i.e. 5, 10, 15 and 25 years),
3) the power rating,
4) the load,
5) the length of time in service since maintenance has been carried out
6) fluids from transformers which have arced or discharged while in service
7) the effects of transformer KVA/Askarel Fluid volume.

The major aim of this study is to ascertain those conditions which change the basic composition of the PCB-containing fluid particularly with respect to the formation of potentially toxic PCDF impurities. This data will be evaluated along with the physical properties of the fluids (i.e. dielectric strength, moisture content, etc.). The sampling process will attempt to obtain and analyse a sufficient number of PCB fluids so that the potential differences between the seven variables can be ascertained. All of the above samples will be split and stored in the dark at 0° prior to use.

Phase III

The isolation and quantification of PCDF and PCDD as minor constituents in PCB fluids involves a number of important analytical procedures which will be carried out as described. Since the PCDF are the most likely contaminants present the methods will primarily refer to their analysis.

1) PCDF Isolation and Clean-up. The isolation of PCDF from the PCB-containing electrical fluid will be carried out by the methods described in the literature.[1,2] The PCB sample (1g) will be chromatographed on activated Florisil (20 g, 80/100 mesh) and the PCB eluted with hexane (200 ml), hexane:acetone (95:5, 50 ml) and finally acetone (100 ml). The latter fraction contains 90% of the PCDF free from PCB impurities.

2) Identification and Quantitation of PCDF. The isolated PCDF samples will be analyzed by GC and GC-MS to determine the range of molecular species present in the diverse electrical fluids. GC will be carried out on a Hewlett-Packard 5710 chromatograph using electron capture detection with a 6' glass column packed with Ultrabond (RFR Corp) or Aue packing. This technique has been shown to give excellent separation of isomers and results in minimum column bleed on to the mass spectrometer. A VG Micromass 7070 mass spectrometer and data system located at the University of Guelph will be used on a contract basis.

Since there are 75 possible PCDF isomers, most of which cannot or have not been made, the task of quantitation of the mixture becomes prohibitive[2]. Moreover quantitation of the highly toxic 2,3,7,8-tetrachlorodibenzofuran (TCDF) is also difficult since there are 22 possible tetrachlorodibenzofuran isomers, however, TCDF quantitation will be made by the GC method. Quantitation will also be attempted by perchlorinating the mixture to give octachlorodibenzofuran as the sole reaction product. The procedure will be carried out as described by Hutzinger, Safe and Zitko. The method uses the BMC reagent[3] (sulfuryl chloride (1 ℓ), sulfur monochloride (5 g), and aluminum chloride (2.5 g)) which on heating converts the mixture into the single octachloro product. Preliminary experiments will be carried out to determine the optimum conditions for this analysis.

In addition, the presence of other possible products present in PCB-containing fluids (e.g. polychlorinated terphenyls, organotin preservatives) will also be investigated using GC and GC-MS.

Phase IV

The incineration and accidental combustion of PCB are known to produce PCDF by-products which depend on the incineration conditions. Recent work by Buser and colleagues[4] have examined the variable temperature pyrolysis of PCB isomers and commercial PCB (Aroclor 1254). The results indicate that below 700° the pyrolysis products contain measurable quantities of dibenzofuran products whereas above 700° the PCB was destroyed (>99.9% decomposition) with the levels of PCDF isomers being non-detectable.

The experiments which will be carried out will attempt to simulate conditions which would occur during a transformer fire. Several (3-4) representative PCB-containing askarel fluids (including fluid from an arced transformer) which have been analysed during Phase II of this project will be subjected to incineration at a range of temperatures which might be expected during a transformer fire (200-500°C). In addition the incineration will be carried out using low oxygen conditions and ambient air levels. The off-gases will be trapped in a glycol solvent and the particulate collected in a glass fibre filter. The incineration unit is currently available in Dr. Hutzinger's laboratory and the PCDF analysis will be carried out as described in Phase III. The organic extracts of the soot can be obtained by repeated soxhlet extraction with methylene chloride. Extraction of the glycol solvent with hexane will remove the PCDF/PCB gaseous material. Thus the simulated environmental burning will evaluate the formation of the potentially toxic PCDF.

Capability

Wellington Science Associates has the analytical and chemical expertise to carry out these projects. Our personnel have access to PCDF and PCDD isomeric standards, and are well versed and experienced in the analytical methodology which will be required. In addition Dr. Hutzinger has direct experience in the incineration/trapping/analysis experiments. Listed below are research and development projects on PCDF and PCDD which have been carried out by Wellington Science personnel.

1. Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. Chemos. 6, 455-460 (1977).

2. Mass and Ion Kinetic Energy Spectra of Some Chlorinated Dibenzo-p-dioxins.
Anal. Chem., 47, 327-329 (1975).

3. Exhaustive Chlorination as a Technique in the Analysis of Aromatic Hydrocarbons. J. Assoc. Offic. Anal. Chem., 56, 982-986 (1973).

4. Photochemical Degradation of Di- and Octachlorodibenzofuran.
Environ. Health Persp., 5, 267-271 (1973).

5. Analysis of Chlorinated Aromatic Hydrocarbons by Exhaustive Chlorination. Quantitative and Structural Aspects of Perchloroderivatives of Biphenyl, Naphthalene, Terphenyl, Dibenzofuran, Dibenzodioxin and DDE.
Environ. Anal. Chem., 2, 95-106 (1972).

6. An Assessment of the Effects of Enzyme Inducers on Aryl Hydrocarbon Hydroxylase Activity.
Res. Commun. Chem. Pathol. and Pharmacol., 18, 59-66 (1977).

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1. J.A.G. Roach and I.H. Pomerantz, Bull. Environ. Contam. Toxicol. 12, 338 (1974).

2. M. Morita, J. Nakagawa, K. Akiyama, S. Mimuraand, N. Isono, Bull. Environ. Contam. Toxicol. 18, 67 (1978).

3. O. Hutzinger, S. Safe and V. Zitko, Environ. Anal. Chem. 2, 95 (1972).

4. H.R. Buser, H.P. Bosshardt and C. Rappe, Chemos. 1, 109 (1978).

5. A. Poland, E. Glover, A.S. Kende, M. DeCamp and C.M. Giandomenico, Science 194, 627 (1976).