INVESTIGATION OF POTENTIALLY HAZARDOUS BYPRODUCTS FORMED FROM PCB'S DURING THE ADELAIDE STREET TRANSFORMER FIRE

This report summarizes the efforts of the MOE Laboratory Services Branch and MOE Central Region to investigate the possibility of formation of toxic oxygenated compounds by the partial combustion of PCBs during the fire at 60 Adelaide Street, December 9th, 1977.

Laboratory Services Branch
February 9th, 1978.

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SUMMARY

(1) MOE Laboratory Services Branch has analyzed a range of samples from the location of the Adelaide Street fire to determine the level of PCB contamination;

(2) In conjunction with the above analyses a sample of soot from the fire scene, and a sample of transformer fluid have been examined for the presence of chlorodibenzo furans and chlorodioxins;

(3) These tests were carried out on an emergency basis, and are the first tests of this type carried out by MOE laboratories. No standards are yet on hand for comparative evaluation, and calibration. Estimates of concentrations present in the samples are thus tentative. Special instrumentation was acquired (gc/ms) and set up in mid January, 1978 to begin the experimental work;

(4) The presence of one tetrachlorodibenzo furan in the soot sample has been positively confirmed. The estimated concentration in soot is 2.5 ppm (possible range 0.5-4.5 ppm). A range of other chlorodibenzo furans have been tentatively identified in the soot sample. Estimated total concentration of these other furans 5 ppm (range 0.7-10 ppm). Positive confirmation of the identity of these compounds is not yet possible and further analytical work has to be carried out.

(5) Trace levels (0.05 ppm) of the tetrachlorodibenzo furan was tentatively identified in the sample of transformer oil from the site of the fire;

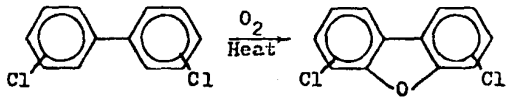
(6) No positive identification of any dioxins (chlorodibenzo dioxins) in any samples from the Adelaide Street fire has yet been obtained.

Introduction

During the period commencing December 9th, 1977, the Laboratory Services Branch was required to provide analytical support, and technical information for the investigation, monitoring and decontamination procedure resulting from the Ontario Hydro transformer fire at 60 Adelaide Street, Toronto. Analyses were carried out on soot, solvent, swabs, air samples and other materials for PCBs.

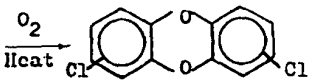
At the same time, it was considered necessary to carry out experimental investigations into the possibility of formation of oxygenated bi-products from PCBs during the fire.

Since furans are known to be produced in PCBs, both as a byproduct of manufacture, and also after long term use at elevated temperature, it was decided to check for the presence of these materials, and the related compounds - dioxins.



PCB Chlorodibenzofuran

-known product



Chlorobenzodioxin

-possible product

Toxicity

Furans and Dioxins are very toxic compounds. Dioxins are known to be powerful teratogens (cause birth defects).. Brief reviews of the toxicity, known modes of production, and environmental behaviour are given in appendices A & B.

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The presence of chlorodibenzofurans in trace levels in new PCB fluids has been well documented (1-3). Greatly enhanced levels of chlorodibenzofurans have also been documented in used PCBs (4). It is believed that these impurities and not PCB itself, were responsible for the outbreak of "YUSHO" disease in Japan in 1968, when a large number of people were poisoned by rice oil contaminated by PCBs (5). To date, no reports have been made of the presence of chlorodibenzodioxins in new or used PCB fluids.

No reports have yet been published to indicate that these toxic materials are formed during fires involving PCBs. However, conditions during the Adelaide St. fire were such that formation was considered possible - high temperatures with electrical arcing, partial combustion with limited oxygen supply, vaporized PCBs.

Experimental work was initiated to check out this possibility of the formation of chlorinated dibenzofurans and dibenzodioxins. A sophisticated high sensitivity Gas Chromatograph/Mass Spectrometer (GC/MS) with capillary column capability was installed during January, 1978 for use in this project. This instrument provides the necessary separation capability, positive identification, and high sensitivity quantitative measurement necessary for analysing trace levels of chlorodibenzofurans and chlorodibenzodioxins.

Due to the lack of proper handling facilities for materials of this extreme toxicity, and the fact that staff has no previous experience of working with them, it was necessary to proceed with extreme caution, and restrict present work on this project to the minimum neccessary to obtain this data.

Literature searches provided a relatively comprehensive set of sample handling, extraction, cleanup and separative techniques for isolating chlorodibenzofurans and chlorodibenzo-

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It was decided to analyze soot from the walls of the building which contained up to 10,000 ppm of PCB residue (wet weight) and which was also a strong adsorbent for the compounds of interest.

A sample of soot was extracted, cleaned up, the compounds of interest separated from PCBs by column chromatography, and the appropriate column eluate fractions analysed first by gas chromatography using electron capture detection, then by GC/MS in both full spectrum scanning mode and selected ion monitoring modes. A full description of the analytical techniques used, and results obtained can be found in Appendix C.

At the same time that the soot extracts were analysed, samples of new PCB and used PCB fluid from the transformer at 60 Adelaide St. were also analysed using the same techniques.

Results

The soot extracts were shown to contain many polynuclear hydrocarbons which, in the full spectrum scanning mode, masked most of the other components present. However, one full confirmatory mass spectrum was obtained for an oxygenated product (Fig. 4). This spectrum gave an excellent match with published spectra for tetrachlorodibenzofuran (Fig. 5).

Selected ion monitoring of ions characteristic of chlorodibenzofurans and chlorodibenzodioxins gave good confirmatory evidence of the presence of di-, tri-, tetra-, penta-, and hexa-chlorodibenzofurans, but insufficient evidence for positive confirmation of the presence of chlorodibenzodioxins.

Analysis of new PCB similar to that from the Adelaide St. transformer showed no trace of chlorodibenzofurans or chlorodibenzodioxin. Analyses of used PCB from the Adelaide St. transformer showed traces of chlorodibenzofurans.

These levels of chlorodibenzofurans were much lower than the levels found in the PCB residues from the soot-extract. This would indicate that the oxygenated products were formed during the fire, and did not originate directly from the used PCB fluid as was the case in the Japanese "YUSHO" incident.

Estimated dibenzofuran concentrations are shown in Table 1.

TABLE 1.

CHLORINATED DIBENZOFURANS IDENTIFIED BY GC/MS AND THEIR ESTIMATED CONCENTRATIONS IN DIFFERENT SAMPLES

Retention Time (min.)	Tentative Identity[a]	Estimated Concentrations (ppm) Wet Soot Sample	Transformer Oil	Arochlor 1260 Std.
6.3	Cl_2-F	0.02-0.2	N.D.	N.D.
8.3	Cl_3-F	0.2-1.6	N.D.	N.D.
9.9	Cl_4-F[b]	0.5-4.7	0.01-0.1	N.D.
11.1	Cl_3-F	0.1-0.9	N.D.	N.D.
11.6	Cl_5-F	0.4-3.7	N.D.	N.D.
12.8	Cl_4-F	0.1-1.2	N.D.	N.D.
13.1	Cl_5-F	0.03-0.3	N.D.	N.D.
13.1	Cl_6-F	0.01-0.05	N.D.	N.D.
Estimate of Total PCDF in sample =		1-13 ppm	0.01-0.1 ppm	N.D.
Concentration of PCB in sample =		1%	50%	100%
Estimate of Total PCDF per PCB present =		100-1300 ppm (median = 600 ppm)	0.02-0.2 ppm (median = 0.1 ppm)	N.D.

N.D. = not detected

a F = dibenzofuran

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b = Positive confirmation on the basis of a full mass spectrum.

All values are reported relative to weight of soot as obtained from fire site. No correction for moisture content has been made. Approximate soot moisture level 80%.

Investigations were limited by:

1. Lack of pure standard materials necessary for comparison and quantitative calibration. These materials were not ordered previously due to the lack of suitable handling facilities. The quantitative data presented here is an estimate, based on the response factors for standards made up with materials of similar structure to the furans and dioxins (e.g. tetrachlorobiphenyl). Standards have been ordered and will be run in the near future.

2. Lack of an adequate high resolution gas chromatographic column. Since the GC/MS has just been installed the only column available was the test column provided - a 3 ft. OV101 column of low resolving power. Capillary columns will be installed as soon as the system is fully tested and adequate disc based data storage is acquired. Capillary operation will provide the proper separation required to obtain full confirmatory mass spectra for each of the compounds so far identified by selected ion monitoring.

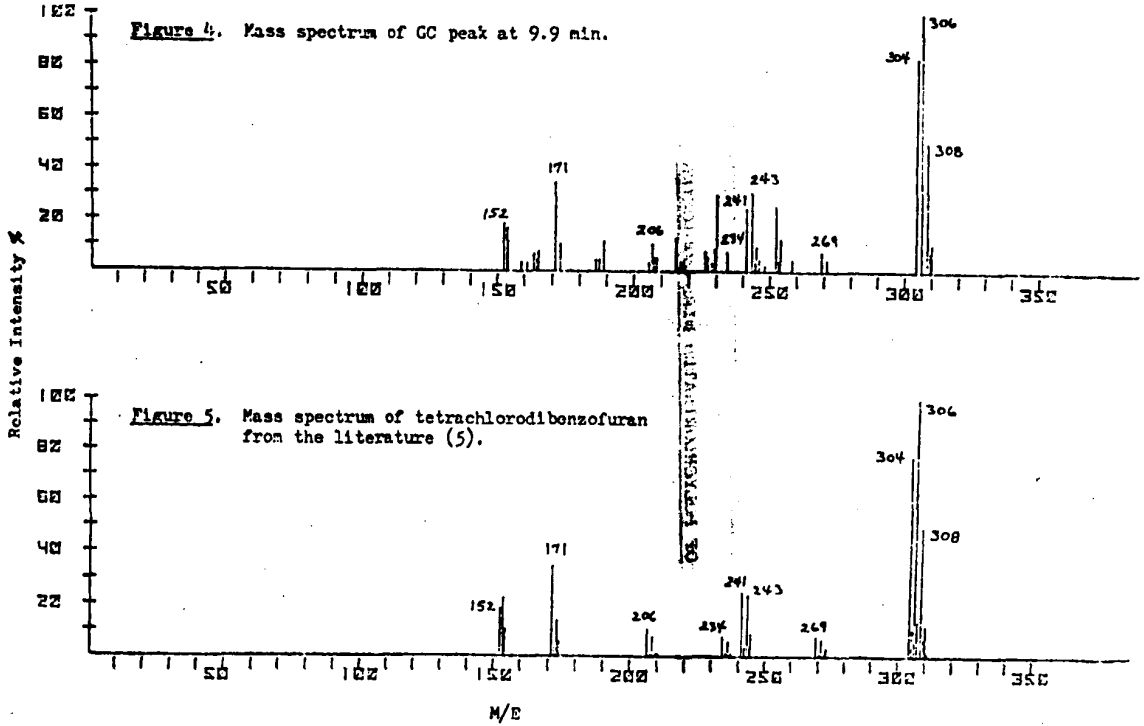

Figure 4. Mass spectrum of GC peak at 9.9 min.

Figure 5. Mass spectrum of tetrachlorodibenzofuran from the literature (5).

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APPENDIX A.

THE TOXICOLOGY AND ENVIRONMENTAL BEHAVIOUR OF POLYCHLORINATED DIBENZODIOXINS

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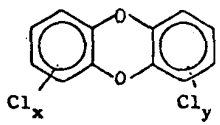
DIOXINS

The name dioxins refer to a group of chemicals of the chlorodibenzo dioxin family.

They have the structure:

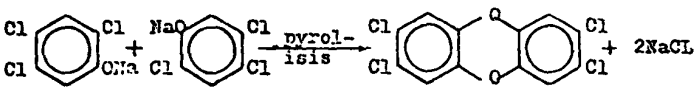


The benzene rings can be substituted with chlorine atoms resulting in many possible isomers, 75 in all. In general, only 5 or 6 have been made. Dioxins have been identified as impurities formed in the manufacture of some chlorinated phenols and chlorophenoxy acid herbicides.[1] They have recently been identified in products resulting from an explosion in a chemical plant manufacturing the germicide "Hexachlorophene".

Dioxins have very low solubilities in water 0.6 ug/l, (1).

OCCURRENCE

Dioxins can occur as impurities in the manufacture of some chlorinated phenols and chlorinated phenoxy acids herbicides. Reaction occurs when a chlorophenol condenses with itself to form a dioxin.



In the manufacture of 2,4,5,T (2,4,5-tri chlorophenoxy acetic acid) a common herbicide from trichlorophenol, certain reactions and high temperatures are required. Under ideal condition, 2,4,5,-T will be produced.

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If the conditions are wrong, a small amount of chlorophenol will combine with itself to form a molecule known as 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD). This material is extremely toxic.

Analysis of commercial 2,4,5-T formulation for dioxin contamination over a 7 year period indicated levels of 0.01 - 1.9 ppm (1). Tetra and penta-chlorophenols contained >10 ppm of dioxins (4).

Thermal decomposition of wood treated with pentachlorophenol produced no dioxins in the residue. However, dioxins were formed if the sodium pentachlorophenate was used instead of the parent phenol. (6). Dioxins do not occur in the manufacture of 2,4-D herbicides.

BIO-CONCENTRATION-PERSISTANCE

The most toxic dioxin, TCDD has been found to have the following environmental effects.

a. It is not leached vertically from a wide variety of soils.
b. Plants have no significant uptake of TCDD when grown in contaminated soil.
c. TCDD has a half life of about 1 year.
d. TCDD is not translocated from a point of application on a leaf surface to other plants parts.
e. TCD is less persistent than most chlorinated hydrocarbon insecticides but is more persistent than 2,4,5,-T. TCDD at 1 ppm in soil is 10^6 greater than the amount that would be found in soil receiving 2,24kg/ha of 2,4,5,-T with a contamination level of .1 ppm TCDD (1).
f. Dioxins are not biosynthesized by condensation of chlorophenols in soils, nor are they photoproducts of 2,4-dichlorophenol.
g. Photodecomposition is insignificant on dry soil surfaces.

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Extracts of 19 bald eagles from locations in the United States were examined for dioxin residues. No dioxins were detected at a level of <50 ppb. (4)

Analysis of fish taken in Viet Nam which was subjected to 2,4,5-T applications indicated levels of TCDD ranging from 0.07 - 0.81 ppb. (5).

TOXICITY

Studies on the toxicities of chlorodibenzo-dioxins have resulted in the following conclusions (3).

1. 2,7-dichlorodibenzo-p-dioxin (DCDD) and octachlorodibenzo-p-dioxin (OCDD) have low acute toxicity. No deaths occured in rats given oral doses of 1g/kg.

2. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has an unusually high toxicity, LD_{50} ranged from 0.6 ug/kg for male guinea pigs to 115 ug/kg for rabbits.

   Death following treatment with a single dose of 2,3,7,8-TCDD is often delayed for several weeks.

3. Hexachlorodibenzo-p-dioxin (HCDD) is highly toxic, but less toxic than TCDD. The lethal dosage ranges from mg/kg for HCDD to ug/kg for TCDD.

4. All chlorodibenzo-dioxins are not alike in their toxicological properties. Isomers of the same dioxin vary in toxicological properties, making it important to identify them specifically. 2,3,7,8-TCDD is high embryotoxic and a potent acnegen. 1,2,3,4-TCDD is neither embryotoxic nor acnegenic.

5. 2,3,7,8-TCDD and HCDD were found to be acnegenic, highly embryotoxic, caused liver necrosis, and were positive for chick edema factor.

6. 2,7-DCDD and OCDD were not chloroacnegenic, and caused neither tetratogenicity or embryotoxicity at doses of 100 mg/kg/day. They were both low in acute oral lethality 1g/kg for mice. OCDD was negative for the chick edema factor.

7. TCDD at dosage levels of 50 ug/kg body weight regularly produced lethal liver necrosis in rabbits (4).

8. 2,3,7,8-TCDD was found to be teratogenic in laboratory animals causing such fetal defects as lack of heads and eyes, cystic kidneys, cleft palates and abnormal livers. (7).

9. 2,3,7,8 has been found to be mutagenic to certain bacterial systems caused by its intercalation with DNA (8).

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APPENDIX B.

THE TOXICOLOGY AND ENVIRONMENTAL BEHAVIOUR OF POLYCHLORINATED DIBENZOFURANS

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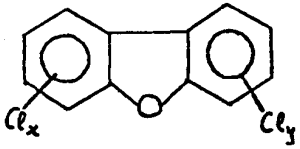
POLYCHLORINATED DIBENZOFURANS

Polychlorinated dibenzofurans (PCDF) have the general formula:



Dibenzofurans are a byproduct in the manufacture of PCB's; in particular the formation of 245 2'4'5' hexachlorobiphenyl (4). They are also found, along with chlorodioxins, in commercial preparations of pentachlorophenol (3) and Hexachlorobenzene (14). PCDF concentrations in PCB's have also been shown to increase when the PCB's are heated in the presence of oxygen (5).

Photodecomposition of the lower (di, tri and tetra chloro) PCB isomers have also been shown to produce dibenzofurans, which themselves then undergo photo decomposition with half lives of days to months depending on the degree of chlorination (6).

The levels of chlorodibenzofurans in PCB fluids, after prolonged use, has also been shown to increase markedly under certain conditions.

Toxicology:

Polychlorinated dibenzofurans are known to be highly toxic substances. Chick embryo bioassays have demonstrated that the ability of 2,3,7,8, tetrachloro- and 2,3,4,7,8 pentechloro dibenzofurans to affect induction of aryl hydrocarbon hydroxylase is comparable to that of 2378 tetrachloro dibenzodioxin (TCDD) (7). The latter compound is known for its high acute toxicity and strong teratogenicity and mutagenicity (10,11).

A single oral dose of 0.5 - 1.0 mg/kg of a PCDF was found to be lethal to rabbits (1).

As noted earlier dibenzofurans have been detected as impurities in various formulations containing PCB, and have been shown to be produced as trace byproducts in the manufacture of PCB's (1).

They were shown to be present in the Japanese PCB product Kaneclor 400 (Kaegafuchi Chemical Co.) which has been identified asthe causative agent for the outbreak of "Yusho" or rice oil poisoning in 1968 in Japan (2). The ingestion of KC400 contaminated rice oil (average of 2 gms KC400 ingested per Yusho patient) caused "Yusho" disease characterized by follicular accentuation, acneform eruptions, anilund skin pigmentation and hypersecretion of the Meikonian gland. An abnormal incidence of stillborn babies or birth defects (including cleft palates, nail and skin pigmentation and swelling of eyelids) was also reported for mothers who had ingested the contaminated rice oil.

The majority of these "Yusho" effects have now been ascribed to the chlorinated dibenzofurans present in the KC400 (8,9).

Levels of PCDF's in a sample of new KC400 were reported to be in range of 20 ppm, while the actual used KC400 product in the "Yusho" incident had levels in excess of 1.1% PCDF, due to excessive use and heating in the "closed" PCB system. This would indicate individual total human exposure levels for Yusho patients of approximately 20 mg of PCDF (5).

Environmental Behaviour & Occurrence

Both the chlorinated dibenzofurans and dibenzodioxins are unstable to light in the presence of organic substrates (6). Even if these compounds were generated under environmental conditions, light provides a mechanism for their rapid destruction. Thus far, PCDF's have not been detected (at levels of 0.01 ug/gm or less) in such environmental samples as the muscle of white shark, eggs of double crested cormorants and Herring gulls, muscle of eel and chain pickerel and in commercial samples of herring oil and groundfish - herring fish meal (15).

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APPENDIX C.

ANALYSIS OF MATERIALS FROM THE ADELAIDE STREET TRANSFORMER FIRE FOR THE PRESENCE OF POTENTIALLY HAZARDOUS BYPRODUCTS FORMED FROM PCBS

Introduction

The recognition of the high toxicity and mutagenicity of chlorinated dibenzofurans (PCDFs) and dibenzodioxins (PCDDs) has led to the publication of many articles on the determination of these substances in environmental samples and commercial preparations of pesticides. The technique most widely used for this analysis is combined gas chromatography/mass spectrometry (GC/MS). The major problem in the analysis of these compounds in environmental samples at trace levels is the sample matrix, which may contain many substances that can interfere in usual methods of analysis. Only GC/MS has the high sensitivity and selectivity required for such determinations.

In this particular problem, we have a sample of soot, formed during the combustion of transformer materials, which contains in addition to carbon, a large amount of PCBs (Arochlor 1260) and organic combustion products.

The experiment described below attempted to determine if there are any detectable traces of PCDFs and PCDDs in the soot sample and in samples of the original transformer oil and pure PCB preparations. Several studies have already been published on the determination of PCDFs and PCDDs in the presence of PCBs (1-6). The procedure for sample clean-up described below is a slight modification of the method of Roach (1), as suggested by Hutzinger et al (2).

Experimental

A sample of soot from the 60 Adelaide St. fire (400 mg wet, 106 mg dried) was extracted with 50 ml benzene in a Soxhlet extractor for four hours. The benzene was evaporated from this extract to give a yellow oil.

This was then dissolved in 1 ml of hexane prior to column chromatography. Samples of transformer oil (90 mg) and Arochlor 1260 standard (4 mg) were simply weighed and dissolved in 1 ml of hexane.

The chromatographic procedure used for sample clean-up is indicated in Figure 1. Samples were applied to a Florisil column (250 mm x 7.5 mm ID, previously washed with 100 ml hexane) and then eluted in three fractions: (1) 100 ml hexane; (2) 50 ml 5% ether/hexane; and (3) 50 ml 25% ether/hexane. Fraction 2 was evaporated and dissolved in 1 ml of 2% CH_2Cl_2/-hexane. This solution was applied to a micro-column of activated basic alumina (50 mm x 4 mm I.D., previously washed with 20 ml 2% CH_2Cl_2/hexane) and eluted into two fractions: (4) 10 ml 2% CH_2Cl_2/hexane; and (5) 10 ml 50%/CH_2Cl_2/hexane. According to the literature, Fraction 5 should contain any PCDFs and PCDDs present in the samples. A blank was also run through all stages of sample clean-up.

Gas chromatography was performed on a Tracor GC with an electron capture detector (ECD) and a 1% Dexil 300 column (6 ft. x 2 mm ID.) operated at 200° isothermal. GC/MS was performed with a Hewlett-Packard 5992A instrument using a short 3% OV-101 column (2 ft x 2 mm ID). The temperatures were as follows: injector - 250°; jet interface - 250°; ion source - 150°; and column oven - 120° for 2 min., then programmed 10°/min to 250°. The mass spectrometer was operated in either the full spectrum scanning mode or with selected ion monitoring (SIM). Table 1 lists the ions characteristic of PCDFs and PCDDs that were monitored in the SIM mode. Confirmation of a species involved observation of each ion in the molecular ion cluster of a compound, along with the correct relative abundance. Estimation of concentrations of various species with the SIM mode was performed by calibrating the instrument response with compounds of similar structure (individual chlorinated biphenyls). This provides only an approximate quantitation; accurate determinations require pure standards.

FIGURE 1.

SCHEME FOR ISOLATION OF PCDFs AND PCDDs

FROM SAMPLES AND CONTAMINATING PCBs

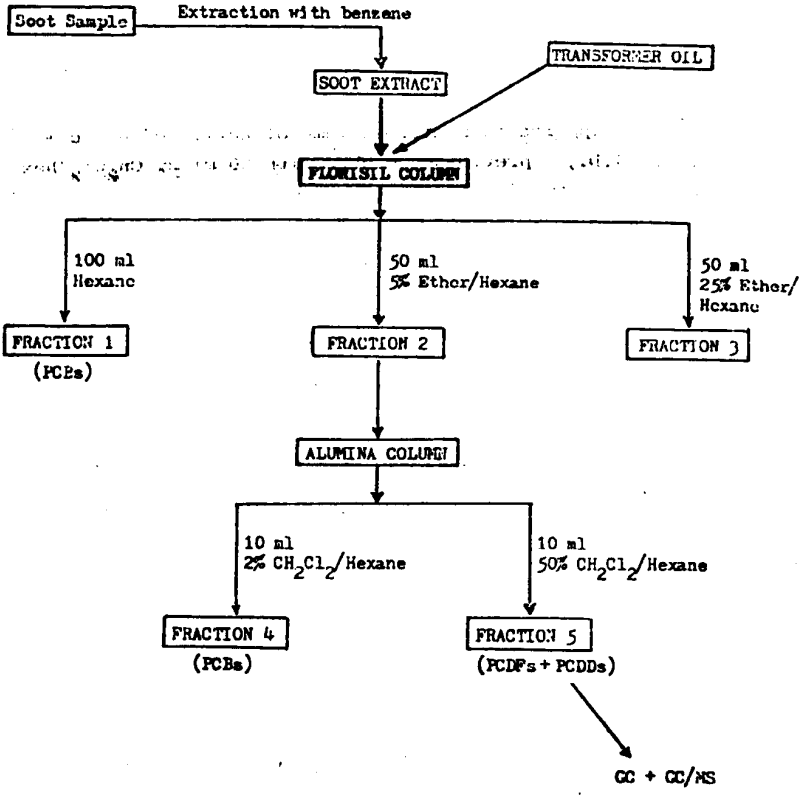

TABLE 1.

SELECTED IONS MONITORED FOR THE DETECTION OF CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS

Compound [a]	Ions Monitored: m/e (Assignment) % RI Expected		
	# 1	# 2	# 3
Cl_2-F	236(M)100.	238(M+2)66	240(M+4)11
Cl_3-F	270(M)100.	272(M+2)98	274(M+4)32
Cl_4-F	308(M+2)100	304(M)77	306(M+4)49
Cl_5-F	340(M+2)100	338(M)61	342(M+4)65
Cl_6-F	374(M+2)100	372(M)51	376(M+4)82
Cl_7-F	408(M+2)100	406(M)44	410(M+4)98
Cl_3-D	286(M)100	288(M+2)98	290(M+4)33
Cl_4-D	322(M+2)100	320(M)76	324(M+4)49
Cl_5-D	356(M+2)100	354(M)61	358(M+4)66

[a] F = dibenzofuran; D = dibenzodioxin

Results and Discussion

Analysis of Fraction 5 of the soot extract by GC revealed the presence of a number of components sensitive to electron capture detection and with retention times in the range expected for PCDFs and PCDDs. Figure 2 gives the chromatogram resulting from this GC/ECD analysis. Assignment of peak identities using GC only requires the use of authentic standards, which were not available at the time.

GC/MS analysis in the full spectrum scanning mode provided a great deal more information on the sample compositions. Figure 3 illustrates the total abundance chromatogram of Fraction 5. Most of the peaks were determined to be polynuclear aromatic hydrocarbon (PAHs) by interpretation of spectra. It appears that the clean-up procedure was not selective enough to remove these substances. This is unfortunate because the spectra of the PAHs, which are in high concentrations, mask the spectra of any other components present. However, one peak with a retention time of 9.9 min. was well separated and gave the spectrum shown in Fig. 4. A search of the literature gave an almost perfect match with the spectrum of tetrachlorodibenzofuran illustrated in Figure 5. This is considered a positive identification.

Determination of the presence of other PCDFs and PCDDs by the full scanning mode is not possible at present and must await installation of a higher resolution capillary column and improved clean-up procedure.

In order to avoid interference from the PAHs and to provide an estimate of concentrations, the more selective and sensitive SIM mode of the GC/MS was used for detection. Table 2 lists a number of dibenzofurans tentatively identified by

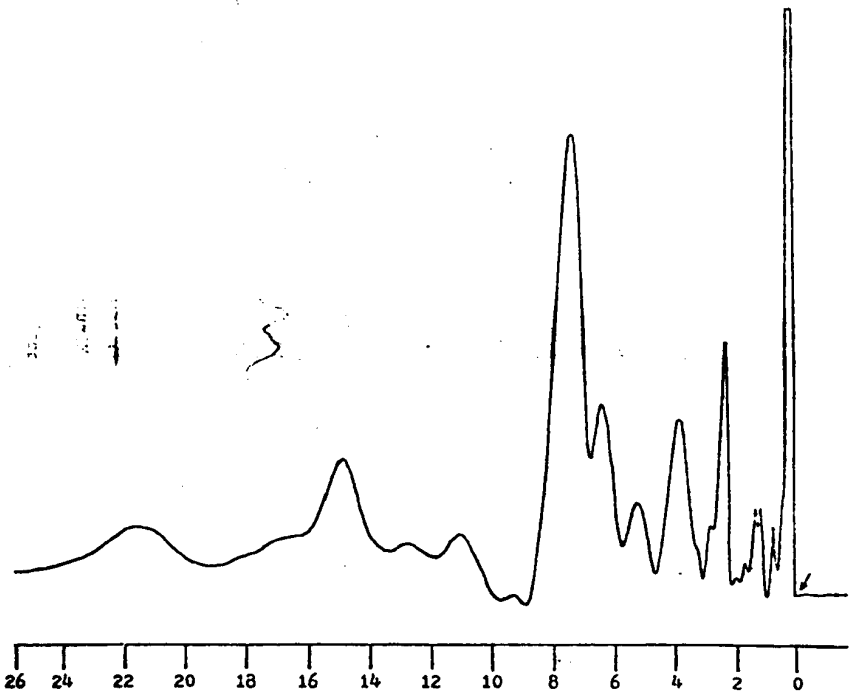

Figure 2. GC-ECD chromatogram of fraction 5 of the soot extract.

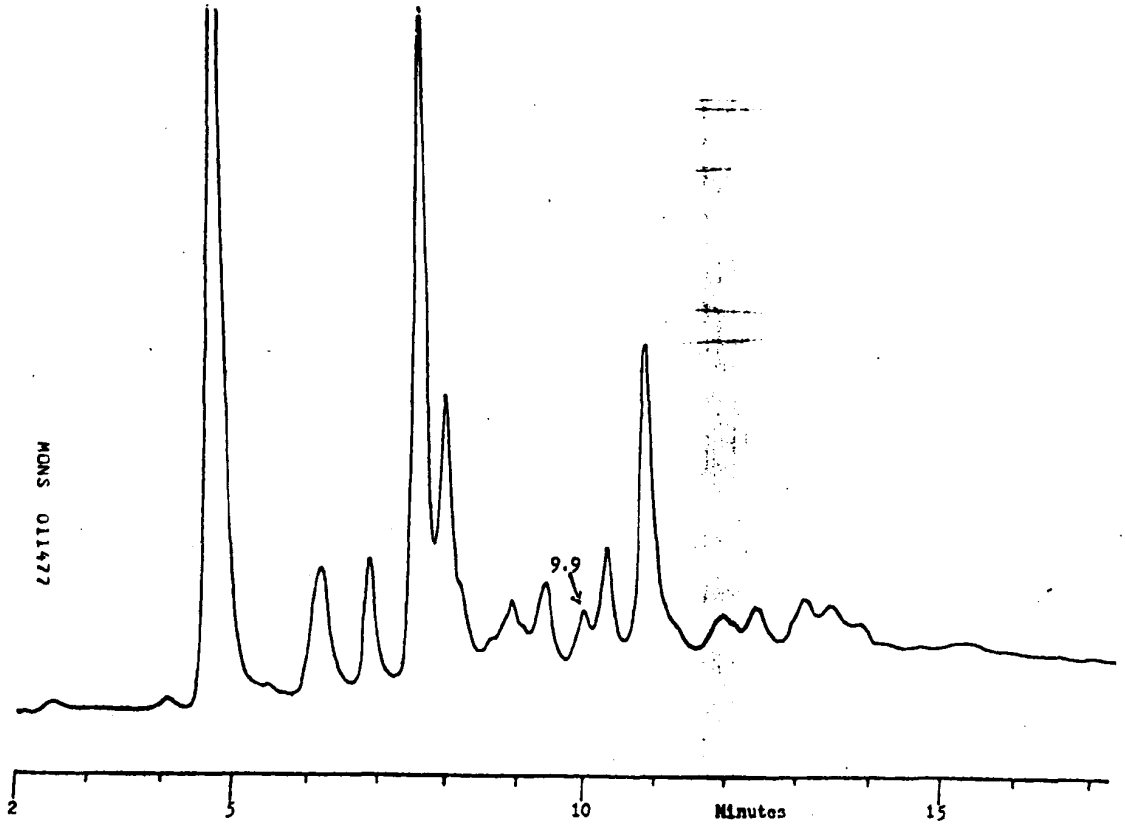

Figure 3. GC/MS total abundance chromatogram of Fraction 5 of the soot extract. The peak marked with an arrow gave the spectrum illustrated in Figure 4.

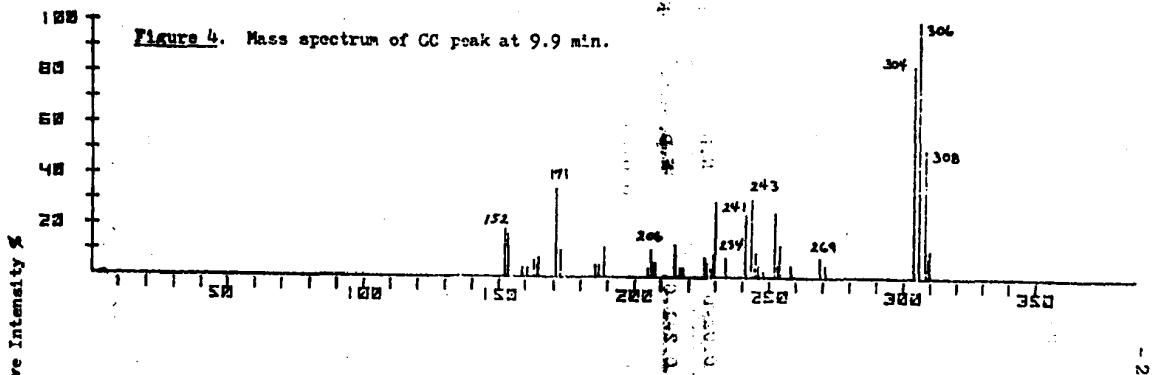

Figure 4. Mass spectrum of GC peak at 9.9 min.

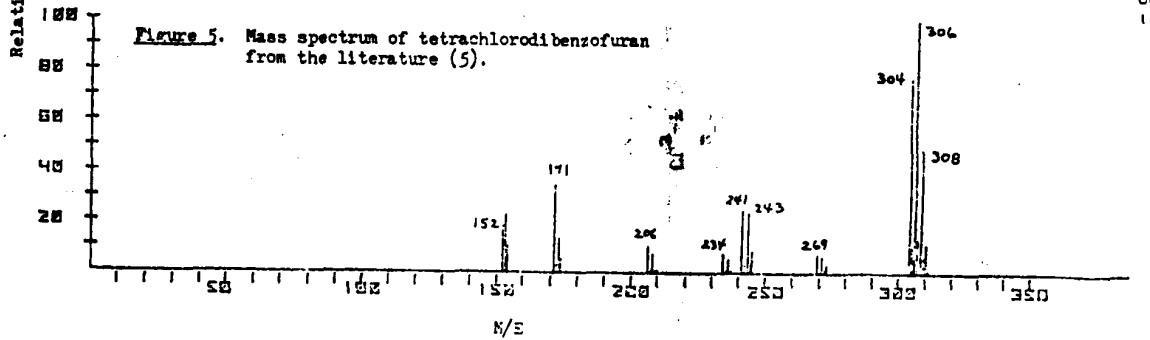

Figure 5. Mass spectrum of tetrachlorodibenzofuran from the literature (5).

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TABLE 2.

CHLORINATED DIBENZOFURANS IDENTIFIED BY GC/MS AND THEIR ESTIMATED CONCENTRATIONS IN DIFFERENT SAMPLES

Retention Time (min.)	Tentative Identity[a]	Estimated Concentrations (ppm) Wet Soot Sample	Transformer Oil	Arochlor 1260 Std.
6.3	Cl_2-F	0.02-0.2	N.D.	N.D.
8.3	Cl_3-F	0.2-1.6	N.D.	N.D.
9.9	Cl_4-F[b]	0.5-4.7	0.01-0.1	N.D.
11.1	Cl_3-F	0.1-0.9	N.D.	N.D.
11.6	Cl_5-F	0.4-3.7	N.D.	N.D.
12.8	Cl_4-F	0.1-1.2	N.D.	N.D.
13.1	Cl_5-F	0.03-0.3	N.D.	N.D.
13.1	Cl_6-F	0.01-0.05	N.D.	N.D.
Estimate of Total PCDF in sample =		1-13 ppm	0.01-0.1 ppm	N.D.
Concentration of PCB in sample =		1%	50%	100%
Estimate of Total PCDF per PCB present =		100-1300 ppm (median = 600 ppm)	0.02-0.2 ppm (median = 0.1 ppm)	N.D.

N.D. = not detected

a F = dibenzofuran

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b = Positive confirmation on the basis of a full mass spectrum.

monitoring the selected ions given in Table 1. Further confirmation of the identities of three compounds-- the di-, tri-, and tetrachlorodibenzofurans (ret. times- 6.3, 8.3, and 9.9 min.)-- was afforded by matching their retention times with those of compounds formed by chlorination of dibenzofuran; and as mentioned above, the tetrachlorodibenzofuran was also positively identified by the full spectrum in Figure 4. Positive confirmations of other compounds require the analysis of standards. These have been ordered; but it should be noted that these cannot be studied until adequate handling facilities are made available.

The presence of chlorodibenzodioxins has not been established as yet, [redacted] experienced in the SIM experiments. Signals were observed for various selected ions monitored, but relative abundance did not agree well with those expected for dioxins. Thus, the determination of chlorodibenzodioxins must await the acquisition of pure standards, the installation of a higher resolution column, and better cleanup procedures.

Table 2 also gives an estimation of concentration of compounds tentatively identified in the different samples analyzed. The results are expressed as a range of values, since it was not possible to determine concentrations accurately without pure standards.

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The most important point to note is the relative amounts of PCDFs in the soot sample versus the transformer oil and a standard of unused PCB (Arochlor 1260). No traces were detected in the PCB standard, while only a small concentration (0.1 ppm maximum) of a tetrachlorodibenzofuran was observed in the used transformer oil. The soot sample, on the other hand, was found to contain a total concentration of PCDFs in the range of 1 to 13 ppm. Based on the amount of PCB in the samples (1% in the wet soot; 50% in the transformer oil), this represents up to a 6000-fold difference in concentrations. This indicates that the oxygenated products were formed during the fire and did not originate directly from the transformer oil.

Conclusions

A number of oxygenated products of PCBs have been observed in the soot sample at far higher concentrations than in the transformer oil prior to the fire. One compound was positively identified: tetrachlorodibenzofuran. Di-, tri-, penta-, and hexa-chlorodibenzofuran were tentatively identified. There is no evidence as yet for the presence of chlorinated dibenzodioxins. Determination of the latter compounds must await acquisition of authentic standards, the installation of a high resolution capillary column in the GC/MS, and the development of better clean-up procedures.

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